1341275

# PATENT SPECIFICATION

(11) 1341275

DRAWINGS ATTACHED

(21) Application No. 24278/71 (22) Filed 19 April 1971
(31) Convention Application Nos. 21994 and 21995
(32) Filed 17 March 1970
(31) Convention Application Nos. 64344 and 64345
(32) Filed 24 July 1970
(31) Convention Application Nos. 97132 and 97133
(32) Filed 6 Nov. 1970 in
(33) Japan (JA)
(44) Complete Specification published 19 Dec. 1973
(51) International Classification C08F 15/04, 1/42
(52) Index at acceptance
C3P 13D1A 13D1B 13D1X 13D2B 13D2C 13D2X 13D5A 13F3 13FX 13G4B 13G4X 13G6 13G7A 13G7BX 13G7C 13G7X 13G7Y 13G8A 13G8X 13G8Y 13H3 13K2A 13K2B 13K3A 13N1 13N4 13R2B 13R3A 13T4

(19) THE PATENT OFFICE LONDON

## (54) A PROCESS FOR PREPARING AN ALTERNATING COPOLYMER OF AN $\alpha$-OLEFIN AND A CONJUGATED DIENE

(71) We, MARUZEN PETRO-CHEMICAL CO., LTD., a Japanese corporate body, of 25—10, Haccho-bori 2-chome, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for preparing an alternating copolymer of an $\alpha$-olefin having the general formula of $CH_2CHR$ wherein R represents a $C_1$—$C_{12}$ hydrocarbon radical selected from the group consisting of alkyl, cycloalkyl, aryl and aralkyl radicals and a $C_4$—$C_{12}$ conjugated diene and a novel alternating copolymer of a $C_4$—$C_{12}$ conjugated diene and said $\alpha$-olefin.

In order to obtain new and useful synthetic elastomers, many attempts have been made to produce an alternating copolymer of a conjugated diene and an $\alpha$-olefin. However, the copolymerization reaction is very difficult and, in general, it is not easy to produce even a random copolymer of conjugated diene and $\alpha$-olefin by an ionic catalyst.

For example, Belgian Patent 546,150 reports a process for preparing an amorphous copolymer of butadiene and an $\alpha$-olefin having more than 3 carbon atoms by using a catalyst system of trialkylaluminum and titanium tetrachloride at 50°C. The copolymer was determined to be amorphous from their X-ray measurements. The chemical configuration of the copolymer is not stereospecific. On the other hand, for example, an alternating copolymer of butadiene and propylene is also shown to be amorphous from its X-ray spectrum at room temperature, but it is a stereospecific copolymer and therefore it can crystallize on stretching or on cooling.

British Patent 1,026,615 claims a process for preparing a random copolymer of butadiene and propylene by forming a catalyst system of trialkylaluminum and titanium tetrachloride in the presence of propylene, and then adding butadiene to the catalyst system. According to the patent, the propylene content of the copolymer was much higher than that of the copolymer prepared by the catalyst system formed in the absence of propylene. The patent also describes that analysis has shown that the copolymer obtained is a random copolymer and not block copolymer, but there are shown no experimental results which support the assumption.

British Patent 1,108,630 shows a process for preparing a rubbery random copolymer of butadiene and propylene of high molecular weight with high content of propylene by using a three components catalyst system consisting of trialkylaluminum, iodine and a compound having the general formula of $TiBr_nCl_{4-n}$ wherein n is zero or an integer of 1 to 4. The microstructure of butadiene unit and the content of propylene unit in the copolymer are shown in the patent. But there are shown no experimental results which support the assumption that the copolymer should be a random copolymer of butadiene and propylene. A random copolymer of butadiene and propylene was also prepared by using a cata-

[*Price 25p*]

lyst system consisting of triethylaluminum, titanium tetrachloride and polypropylene oxide. Polypropylene oxide was used as a randomizer and a copolymer of butadiene and propylene prepared by the catalyst system of triethylaluminum and titanium tetrachloride was shown to be block type from the results of oxidative decomposition reaction of the copolymer (Paper presented at 2nd Symposium on Polymer Synthesis, Tokyo. October 5, 1968, The Society of Polymer Science, Japan).

At any rate, all of the methods described above relate to the methods for preparing a nonstereospecific or atactic copolymer. On the other hand, an alternating copolymer is stereospecific and therefore these methods are not pertinent to the process of this invention.

Recently, Furukawa, et. al. reported a process for preparing an alternating copolymer of butadiene and an $\alpha$-olefin by using vanadyl (V) chloride—diethylaluminum monochloride—triethylaluminum catalyst system (22nd Annual Meeting of Japan Chemical Society, Tokyo, March 31, 1969; J. Polymer Sci., *B7*, 671 (1969).

The methods for preparing an alternating copolymer of butadiene and an $\alpha$-olefin by using an organoaluminum compound—vanadium (IV) chloride or vanadium (V) oxychloride—organic peroxide or chromium (VI) oxychloride catalyst system (British Patent 1297165), an organoaluminum compound—a vanadium compound having no vanadium-halogen linkage—a halogen compound catalyst system (British Patent 1296998; J. Polymer Science, *B7*, 613 (1969)) and an organoaluminum compound—a vanadium compound having vanadium-halogen linkage—a compound having M—OR (M is an atom whose electronegativity is less than 2.2 and R is a hydrocarbon radical) linkage catalyst system (British Patent 1304038) were all proposed by us previously.

In short, the catalyst systems for alternating copolymerization described above employ an organoaluminum compound and a vanadium compound as indispensable elements of the catalyst systems. The microstructure of butadiene units in the alternating copolymer of butadiene and an $\alpha$-olefin prepared by these catalyst systems was almost all trans-1,4-configuration, occasionally involving minor amounts of 1,2-configuration.

On the other hand, the most recently, we proposed the process for preparing an alternating copolymer of butadiene and an $\alpha$-olefin by using the three components catalyst system of an organoaluminum compound titanium tetrahalide and a carbonyl group containing compound (British Patent 1310943). The alternating copolymer prepared by this catalyst system contains considerable amounts of cis-1,4-configuration butadiene unit, occasionally involving minor amounts of cis-1,2-configuration and moreover molecular weight of the alternating copolymer is remarkably higher than that of the one prepared by the organoaluminum-vanadium compound type catalyst system described above.

Accordingly, an object of the present invention is to provide a process for preparing an alternating copolymer of a conjugated diene and an $\alpha$-olefin having a high molecular weight in a good yield.

It is a further object of this invention to provide a catalyst system giving said high molecular weight alternating copolymer of a conjugated diene and an $\alpha$-olefin in a good yield.

It is a still further object of this invention to provide an alternating copolymer of a $C_4$—$C_{12}$ conjugated diene and an $\alpha$-olefin having the general formula of $CH_2{=}CHR$ wherein R represents a $C_1$—$C_{12}$ hydrocarbon radical selected from alkyl, cycloalkyl, aryl and aralkyl radicals.

In accordance with this invention, we have found that a high molecular weight alternating copolymer of a conjugated diene and an $\alpha$-olefin can be produced in a good yield by using a catalyst system comprising as a first component an organoaluminum compound having the general formula of $AlR_3$ wherein R represents a hydrocarbon radical selected from a $C_1$—$C_{12}$, preferably $C_1$—$C_8$, and more preferably $C_1$—$C_6$, alkyl, cycloalkyl, aryl and aralkyl radicals, as a second component an organic titanium compound having the

$$\mathrm{TiXO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}$$

(R is the same one as described above and X is halogen) structure in the molecule, and optionally as a third component a halogen, a halogen compound (other than the second component) or a mixture thereof.

The alternating copolymers of this invention are rubber-like in character and can be used as polymeric plasticizers, in adhesives and can be vulcanized with sulfur or a sulfur compound to produce vulcanized elastomers.

The organoaluminum compounds which form the first component of the catalyst system used in this invention are defined by the formula $AlR_3$ wherein R is a hydrocarbon radical selected from a $C_1$—$C_{12}$, preferably $C_1$—$C_8$, and more preferably $C_2$—$C_6$, alkyl, cycloalkyl, aryl and aralkyl radicals. Mixtures of these organoaluminum compounds may also be employed. Specific examples of compounds represented by the formula include trimethylaluminum, triethylaluminum, tri-n-propylaluminum, triisopropylaluminum, tri-n-butylaluminum, triisobutylaluminum, tripentylaluminum, trihexylaluminum, tricyclohexyl-

aluminum, trioctyl-aluminum, triphenylaluminum, tri-p-tolylaluminum, tribenzylaluminum, ethyldiphenylaluminum, ethyl di-p-tolylaluminum, ethyl dibenzylaluminum, diethylphenylaluminum, diethyl-p-tolylaluminum and diethyl benzylaluminum. Mixtures of these compounds may also be employed. Of these, it is usually preferred to employ trialkylaluminum compounds.

The organic titanium compounds having the

$$\mathrm{TiXO\overset{\overset{O}{\|}}{C}R}$$

(R is a hydrocarbon radical selected from $C_1$—$C_{12}$, preferably $C_1$—$C_8$, and more preferably $C_1$—$C_6$, alkyl, cycloalkyl, aryl and aralkyl radicals and X is halogen) structure in the molecule and forming the second component of the catalyst system of this invention, by no means limiting, are compounds shown by the general formulae of

$$\mathrm{TiX(O\overset{\overset{O}{\|}}{C}R)_3},$$

$$\mathrm{TiX_2(O\overset{\overset{O}{\|}}{C}R)_2},$$

$$\mathrm{TiX_3(O\overset{\overset{O}{\|}}{C}R)},$$

$$\mathrm{O[TiX_2(O\overset{\overset{O}{\|}}{C}R)]_2},$$

$$\mathrm{O[TiX(O\overset{\overset{O}{\|}}{C}R)_2]_2},$$

$$\mathrm{TiX(OR)—(O\overset{\overset{O}{\|}}{C}R)_2}$$

and

$$\mathrm{TiX(OR)_2(O\overset{\overset{O}{\|}}{C}R)},$$

and mixtures thereof.

A mixture of organic titanium compound having the

$$\mathrm{TiO\overset{\overset{O}{\|}}{C}R}$$

(R is as defined above) structure and having no Ti—X linkage in the molecule and halogen, a halogen compound or a mixture thereof can be used as the second component of the catalyst of this invention, provided that said organic titanium compound can react with halogen, said halogen compound or the mixture thereof to produce an organic titanium compound having

$$\mathrm{TiXO\overset{\overset{O}{\|}}{C}R}$$

structure, *in situ*. Examples of such

$$\mathrm{TiO\overset{\overset{O}{\|}}{C}R}$$

structure containing compounds, by no means limiting, are the compounds shown by the general formulae

$$\mathrm{Ti(O\overset{\overset{O}{\|}}{C}R)_4},$$

$$\mathrm{O[Ti(O\overset{\overset{O}{\|}}{C}R)_3]_2},$$

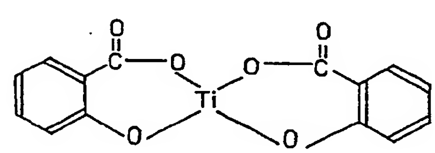
$$\mathrm{Ti(OR)_3(O\overset{\overset{O}{\|}}{C}R)},$$

$$\mathrm{Ti(OR)_2(O\overset{\overset{O}{\|}}{C}R)_2},$$

$$\mathrm{Ti(OR)(O\overset{\overset{O}{\|}}{C}R)_3},$$

$$\mathrm{TiO(O\overset{\overset{O}{\|}}{C}R)_2},$$

and



Examples of R radicals employed in the above organic titanium compounds are, by no means limiting, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, hexyl, cyclohexyl, octyl, phenyl, p-tolyl and benzyl.

The halogen compounds which form the optional third component of the catalyst system of this invention and are also used as the halogen source for transforming the compounds having

$$\mathrm{TiO}\overset{\overset{\displaystyle O}{\|}}{C}\mathrm{R}$$

structure to the second component of the catalyst system are exemplified by compounds showing Lewis acid property such as compounds of the general formulae, $VX_4$ (X is halogen hereinafter the same), $VOX_3$, $WX_6$, $MoX_5$, $CrO_2X_2$, $ZrX_4$, $FeX_3$, $BX_3$, $PX_5$, $SnX_4$, $SbX_5$, $AlOX_3$, $AlX_3$, $Cu_2X_2$, $MnX_2$, $MgX_2$, $ZnX_2$, $HgX_2$, $BiX_3$ and $NiX_2$; Lewis base complex compounds of the above mentioned halogen compounds showing Lewis acid property such as compounds of the general formulae

$$AlX_3.O(C_2H_5)_2,$$
$$BX_3.O(C_2H_5)_2,$$
$$VOX_3.O(C_2H_5)_2,$$
$$FeX_3.O(C_2H_5)_2,$$

$NiX_2.Py$ (Py represents pyridine) and $HgX_2.Py$; organic aluminum compounds having an Al—X linkage such as compounds of $Al(OR)_nX_{3-n}$ (n is a number from 1 to 2 and R is as defined above) and $AlR_nX_{3-n}$ (n is a number from 1 to 2 and R is as defined above); organic transition metal compounds having transition metal—X linkage such as compounds of the general formulae $OV(OR)_nX_{3-n}$ (n is a number from 1 to 2), $Ti(OR)_4X_{4-n}$ (n is a number from 1 to 3), $Zr(OR)_2X_2$, $Zr(OR)_3X$, $OV(C_5H_7O_2)_nX_{3-n}$ (n is a number from 1 to 2), $V(C_5H_5)_nX_{4-n}$ (n is a number from 1 to 2), $V(C_5H_5)_2X$, $OV(C_5H_5)X_2$, $Ti(C_5H_5)_2X$, $Ti(C_5H_5)X_3$, $Ti(C_5H_5)_2X_2$, $(C_5H_5)Ti(OR)X_2$, $(C_5H_5)_2CrX$, $(C_5H_5)Mo(CO)_3X$ and $(C_5H_5)_2IrX_3$; acid halide; compounds having the general formula of

$$\begin{matrix} X \\ \phantom{X} \\ X \end{matrix}\!\!>C=O;$$

the halogenated alkane compounds tert-butyl halide, sec-butyl halide and carbon tetrahalide, or mixtures thereof.

In the preferred embodiment the molar ratio of organoaluminum compound which forms the first component of the catalyst system of the present invention to organic titanium compound which forms the second component of the catalyst system should be in the range of 200 to 1 (200>Al/Ti>1), the optimum ratios will be found between 100 and 2 (100>Al/Ti>2).

In the preferred embodiment, the atomic ratio of titanium atom in the catalyst system of the present invention to halogen atom in the catalyst system should be in the range of 0.01 to 20 (0.01<Ti/X<20), the optimum ratios will be found between 0.02 and 10 (0.02<Ti/X<10).

The $\alpha$-olefin used in this invention is one having the general formula:

$$CH_2=CHR$$

wherein R is a hydrocarbon radical selected from a $C_1$—$C_{12}$, preferably $C_1$—$C_8$, and more preferably $C_1$—$C_6$, alkyl, cycloalkyl, aryl and aralkyl radical. Specific examples of compounds represented by the formula include propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, 4-methyl-hexene-1, 5-methyl-hexene-1, heptene-1, 5-methyl-heptene-1, octene-1, decene-1, vinylcyclohexane, 4-methyl-1-vinylcyclohexane and styrene. Mixtures of these $\alpha$-olefin monomers may also be employed.

The conjugated dienes to be used in the present invention have from 4 to 12 carbon atoms, and typical examples are butadiene, pentadiene-1,3, hexadiene-1,3, isoprene, 2-ethyl butadiene, 2-propyl butadiene, 2-isopropyl butadiene, 2,3-dimethyl butadiene, phenyl butadiene, etc. Among them, butadiene, isoprene and pentadiene-1,3 are preferable. A mixture of them may also be employed.

The molar ratio of conjugated diene to $\alpha$-olefin in the initial monomer composition is not critical, but is usually within the range of 10/1 to 1/100 (10/1>diene/$\alpha$-olefin>1/100), preferably be 5/1 to 1/50 (5/1>diene/$\alpha$-olefin>1/50). It is noteworthy that, for example, when copolymerization reaction proceeds 50% by using a monomer mixture having the initial monomer composition of 1:50, the molar ratio of unreacted conjugated diene to unreacted $\alpha$-olefin at this stage should be 1:99.

The manner for preparing the catalyst system of this invention has not been found to be critical. The organoaluminum compound which forms the first component of the catalyst system and the organic titanium compound which forms the second component of the catalyst system or the organoaluminum compound, the organic titanium compound and the halogen or halogen compound which forms the third component of the catalyst system of the present invention can be mixed per se or they can be mixed in the presence of an organic solvent. If a solvent is to be employed, the aromatic solvents such as benzene, toluene or xylene; the aliphatic hydrocarbons e.g. propane, butane, pentane, hexane, heptane, or cyclohexane; the halogenated hydrocarbon solvents trihaloethanes, methylene halides or tetrahaloethylenes are usually preferred.

In general, the organoaluminum compound which forms the first component of the catalyst system and the organic titanium compound which forms the second component of the catalyst system may suitably be mixed at a temperature within a very wide range from −100°C to +100°C, and preferably from −78°C to +50°C. This temperature is shown as catalyst preparation temperature in the Tables given hereinafter. The halogen

or halogen compound which forms the third component of the catalyst system may suitably be mixed with the other one or two components of the catalyst system of this invention at a temperature within a very wide range from −100°C to +100°C, and preferably from −78°C to +50°C.

The polymerization reaction may suitably be carried out at a temperature within a range from −100°C to +100°C, and preferably from −78°C to +50°C.

The practice of this copolymerization is usually carried out in the presence of an organic solvent or diluent. However, this does not mean that this invention cannot be practiced in the form of bulk polymerization, i.e. without the use of solvent. If it is desired to use a solvent, the aromatic solvents such as benzene, toluene or xylene; the aliphatic hydrocarbons, e.g. propane, butane, pentane, hexane, heptane or cyclohexane; the halogenated hydrocarbon solvents, trihaloethanes, methylene halides or tetrahaloethylenes may also be employed.

At the completion of the copolymerization reaction, the product may be precipitated and deashed by using a methanol-hydrochloric acid mixture. The precipitated product may be further washed with methanol for several times and dried under vacuum.

The catalyst system used in the present invention employs an organoaluminum compound and a titanium compound as main components and in contrast to the alternating copolymer of butadiene and an α-olefin prepared by the organoaluminum-vanadium compound type catalyst system, the butadiene units of the alternating copolymer of butadiene and the α-olefin prepared by the methods of this invention contains considerable amounts of cis-1,4-structure and occasionally involves minor amounts of 1,2-structure. In other words, the structure of the alternating copolymer of butadiene and α-olefin prepared by the method of this invention resembles that of the one prepared by the catalyst system of an organoaluminum compound, titanium tetrahalide and a carbonyl group containing compound (British Patent 1310943).

As shown in Examples 21, 24 and Experiments 1 and 2 of Example 25 in detail, the products obtained in these Examples were determined through many facts as the alternating copolymers of isoprene with propylene, hexene-1, pentene-1 and butene-1 respectively. Also, as shown in Examples 26 and 28 in detail, the products obtained in these Examples were determined through many facts as the alternating copolymers of pentadiene-1,3 with propylene and hexene-1 respectively.

Fig. 1 shows the infra-red spectrum of the typical example of alternating copolymer of isoprene and propylene prepared by the method of this invention; Fig. 2 shows the nuclear magnetic resonance spectrum of the copolymer; Fig. 3 shows the infra-red spectrum of the typical example of alternating copolymer of isoprene and butene-1 prepared by the method of this invention; Fig. 4 shows the nuclear magnetic resonance spectrum of the copolymer; Fig. 5 shows the infra-red spectrum of the typical example of alternating copolymer of isoprene and pentene-1 prepared by the method of this invention; Fig. 6 shows the nuclear magnetic resonance spectrum of the copolymer; Fig. 7 shows the infra-red spectrum of the typical example of alternating copolymer of isoprene and hexene-1 prepared by the method of this invention; Fig. 8 shows the nuclear magnetic resonance spectrum of the copolymer; Fig. 9 shows the infra-red spectrum of the typical example of alternating copolymer of pentadiene-1,3 and propylene; Fig. 10 shows the nuclear magnetic resonance spectrum of the copolymer; Fig. 11 shows the infra-red spectrum of the alternating copolymer of isoprene and propylene prepared by the catalyst system of triisobutylaluminum, vanadium (V) oxychloride and partial hydrolysis product of aluminumtriisopropoxide at −40°C; and Fig. 12 shows the nuclear magnetic resonance spectrum of the copolymer.

The invention will be illustrated with reference to the following Examples.

## Example 1.

The usual, dry, air-free technique was employed and 0.16 millimole organic titanium compound, 6.5 milliliters toluene and 0.2 millimole halogen compound were put successively into 25 milliliter glass bottles at 25°C. Then, the bottles were left alone at 25°C for 10 minutes. Thereafter, the bottles were held in a low temperature bath at −78°C (it corresponds to the catalyst preparation temperature shown in Table 1) and 2.0 milliliters triisobutylaluminum solution in toluene (1 molar solution) and a mixture of 2.0 milliliters liquid propylene, 2 milliliters liquid butadiene and 2.0 milliliters toluene were put successively into the bottles also employing the usual, dry, air-free technique. Thereafter, the bottles were sealed and the contents allowed to copolymerize at −30°C for 16 hours. The results are summarized in Table 1.

The molecular weight of the MEK soluble fraction of the alternating copolymer was lower than that of the MEK insoluble and diethyl ether soluble fraction of the alternating copolymer. Therefore, it is concluded that the yield of the high molecular weight fraction in Exp. No. 4 obtained by the two components catalyst system of

$$Al(iBu)_3—TiCl_3O\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

is lower than that of the ones in Exp. No. 1—3 obtained by the three components catalyst systems of $Al(iBu)_3—TiCl_3OC(=O)CH_3—$halogen compound.

TABLE 1

| Exp. No. | Catalysts* | | | Catalyst preparation temperature (°C) | Polymerization conditions | |
|---|---|---|---|---|---|---|
| | Al(i−Bu)$_3$ (mmol) | Organictitanium compound, $TiCl_3OC(=O)CH_3$ (mmol) | Halogen or halogen compound (mmol) | | Temperature (°C) | Time (hr.) |
| 1 | 2.0 | 0.16 | $SnCl_4$ 0.2 | −78 | −30 | 16 |
| 2 | 2.0 | 0.16 | $BF_3.OEt_2$ 0.2 | −78 | −30 | 16 |
| 3 | 2.0 | 0.16 | $C_6H_5COCl$ 0.2 | −78 | −30 | 16 |
| 4 | 2.0 | 0.16 | —— | −78 | −30 | 16 |

* Al(i−Bu)$_3$: triisobutylaluminium, $BF_3.OEt_2$: boron trifluoride etherate, $C_6H_5COCl$: benzoyl chloride

TABLE 1 (continued)

| | Yield of alternating copolymer of butadiene and propylene | |
|---|---|---|
| | MEK soluble fraction (g) | MEK insoluble, diethyl ether soluble fraction (g) |
| 1 | 0.16 | 1.09 |
| 2 | 0.40 | 0.61 |
| 3 | 0.24 | 0.58 |
| 4 | 0.40 | 0.34 |

Example 2.

The usual, dry, air-free technique was employed and 0.2 millimole organic titanium compound, 6.5 milliliters toluene and 0.5 millimole halogen or halogen compound were put successively into 25 milliliter glass bottles at 25°C. Then the bottles were left alone at 25°C for 10 minutes. Thereafter, the bottles were held in a low temperature bath at −78°C (it corresponds to catalyst preparation temperature shown in Table 2) and 2.0 milliliters triisobutylaluminum solution in toluene (1 molar solution) and a mixture of 2.0 milliliters liquid propylene, 2.0 milliliters liquid butadiene and 2.0 milliliters toluene were put successively into the bottles also employing the usual, dry, air-free technique. Thereafter, the bottles were sealed and the contents allowed to copolymerize at −30°C for 16 hours. The results are summarized in Table 2.

The catalyst systems shown in Ref. 1 and 2 gave no alternating copolymer.

TABLE 2

| Exp. No. | Catalysts* | | | Catalyst preparation temperature (°C) | Polymerization conditions | |
|---|---|---|---|---|---|---|
| | $Al(i-Bu)_3$ (mmol) | Organic: titanium compound, (mmol) | Halogen or halogen compound (mmol) | | Temperature (°C) | Time (hr.) |
| 1 | 2.0 | $O[Ti(OAc)_3]_2$ 0.2 | $AlCl_3.OEt_2$ 0.5 | −78 | −30 | 16 |
| 2 | 2.0 | $O[Ti(OAc)_3]_2$ 0.2 | $AlEtCl_2$ 0.5 | −78 | −30 | 16 |
| 3 | 2.0 | $O[Ti(OAc)_3]_2$ 0.2 | $SnCl_4$ 0.5 | −78 | −30 | 16 |
| 4 | 2.0 | $O[Ti(OAc)_3]_2$ 0.2 | $I_2$ 0.5 | −78 | −30 | 16 |
| Ref. 1 | 2.0 | $O[Ti(OAc)_3]_2$ 0.2 | — | −78 | −30 | 16 |
| 5 | 2.0 | $Ti(Oi-Pr)_2(OAc)_2$ 0.2 | $VOCl_3$ 0.5 | −78 | −30 | 16 |
| 6 | 2.0 | $Ti(Oi-Pr)_2(OAc)_2$ 0.2 | $I_2$ 0.5 | −78 | −30 | 16 |
| Ref. 2 | 2.0 | $Ti(Oi-Pr)_2(OAc)_2$ 0.2 | — | −78 | −30 | 16 |

* $Al(i-Bu)_3$: triisobutylaluminium. $O[Ti(OAc)_3]_2$: $O[Ti(O\overset{O}{\overset{\|}{C}}CH_3)_3]_2$, $Ti(Oi-Pr)_2(OAc)_2$: $Ti_6OCH(CH_3)CH_3]_2.[O\overset{O}{\overset{\|}{C}}CH_3]_2$
$AlCl_3.OEt_2$: aluminium chloride etherate,

TABLE 2 (continued)

| Exp. No. | Yield of alternating copolymer of butadiene and propylene | |
|---|---|---|
| | MEK soluble fraction (g) | MEK insoluble, diethyl ether soluble fraction (g) |
| 1 | 0.24 | 0.25 |
| 2 | 0.15 | 0.10 |
| 3 | 0.01 | 0.08 |
| 4 | 0.07 | 0.32 |
| Ref. 1 | 0 | 0 |
| 5 | 1.46 | 0.74 |
| 6 | 0.11 | 0.06 |
| Ref. 2 | 0 | 0 |

Example 3.

The usual, dry, air-free technique was employed and 8.0 milliliters toluene and varying amounts of organic titanium compound

$$(TiCl_3O\overset{\overset{O}{\|}}{C}C_6H_5)$$

were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a constant temperature bath showing a predetermined temperature (it corresponds to the catalyst preparation temperature given in Table 3 listed below) and varying amounts of organoaluminum compound solution in toluene (1 molar solution) were put into the bottles. Thereafter, the bottles were held in a low temperature bath at −78°C and a mixture of 2.0 milliliters liquid propylene, 2.0 milliliters liquid butadiene and 2 milliliters toluene was put into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 3.

TABLE 3

| Exp. No. | Catalysts* Organoaluminum compound (mmol) | Organic titanium compound, $TiCl_3OC(=O)C_6H_5$ (mmol) | Catalyst preparation temperature (°C) | Polymerization conditions Temperature (°C) |
|---|---|---|---|---|
| 1 | $Al(i-Bu)_3$ 0.25 | 0.10 | −30 | −40 |
| 2 | $Al(i-Bu)_3$ 0.25 | 0.10 | −20 | −40 |
| 3 | $Al(i-Bu)_3$ 0.25 | 0.10 | −10 | −40 |
| 4 | $Al(i-Bu)_3$ 0.25 | 0.10 | 0 | −40 |
| 5 | $Al(i-Bu)_3$ 0.50 | 0.025 | −78 | −30 |
| 6 | $Al(i-Bu)_3$ 0.50 | 0.05 | −78 | −30 |
| 7 | $Al(i-Bu)_3$ 0.50 | 0.10 | −78 | −30 |
| 8 | $Al(i-Bu)_3$ 0.50 | 0.18 | −78 | −30 |
| 9 | $Al(i-Bu)_3$ 0.50 | 0.20 | −78 | −30 |
| 10 | $Al(i-Bu)_3$ 0.50 | 0.23 | −78 | −30 |
| 11 | $Al(i-Bu)_3$ 0.50 | 0.25 | −78 | −30 |
| 12 | $Al(i-Bu)_3$ 0.50 | 0.275 | −78 | −30 |
| 13 | $Al(i-Bu)_3$ 0.30 | 0.10 | −30 | −37 |
| 14 | $Al(i-Bu)_3$ 0.30 | 0.10 | −78 | 20 |
| 15 | $AlEt_3$ 0.50 | 0.20 | −78 | −30 |

* $Al(i-Bu)_3$: triisobutylaluminum, $AlEt_3$: triethylaluminum

TABLE 3 (continued)

| Exp. No. | Polymerization conditions | Alternating copolymer of butadiene and propylene | | | | |
|---|---|---|---|---|---|---|
| | Time (hr.) | Yield (g) | ** Intrinsic Viscosity [γ] (dl/g) | Microstructure of butadiene unit | | |
| | | | | cis (%) | trans (%) | 1,2 (%) |
| 1 | 16 | 1.92 | 3.47 | 11 | 86 | 3 |
| 2 | 16 | 1.89 | 4.31 | 12 | 85 | 3 |
| 3 | 16 | 1.78 | 4.59 | 13 | 84 | 3 |
| 4 | 16 | 1.14 | 4.81 | 22 | 75 | 3 |
| 5 | 16 | 0.13 | — | — | — | — |
| 6 | 16 | 0.34 | — | — | — | — |
| 7 | 16 | 0.77 | — | — | — | — |
| 8 | 16 | 1.41 | 2.01 | 7 | 89 | 4 |
| 9 | 16 | 1.46 | 1.98 | — | — | — |
| 10 | 16 | 1.47 | 1.62 | 6 | 90 | 4 |
| 11 | 16 | 1.02 | — | — | — | — |
| 12 | 16 | 0.64 | — | — | — | — |
| 13 | 17.5 | 1.81 | 3.24 | 12 | 86 | 2 |
| 14 | 25 | 1.21 | 0.62 | — | — | — |
| 15 | 16 | 0.80 | — | — | — | — |

** measured in chloroform at 30°C.

Example 4.

The usual, dry, air-free technique was employed and 8.0 milliliters toluene and varying amounts of organic titanium compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a constant temperature bath showing predetermined temperature (it corresponds to catalyst preparation temperature given in Table 4) and varying amounts of organoaluminum compound solution in toluene (1 molar solution) were put into the bottles. Thereafter, the bottles were held in a low temperature bath at −78°C and a mixture of 2.0 milliliters liquid propylene, 2.0 milliliters liquid butadiene and 2.0 milliliters toluene was put into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature for 16 hours. The results were summarized in Table 4.

TABLE 4

| Exp. No. | Catalysts: Organoaluminum compound (mmol) | Catalysts: Organic titanium compound, $TiCl_3OC(=O)C_6H_5$ (mmol) | Catalyst preparation temperature (°C) | Polymerization conditions: Temperature (°C) |
|---|---|---|---|---|
| 1 | $Al(i-Bu)_3$ 1.00 | 0.23 | −78 | −30 |
| 2 | $Al(i-Bu)_3$ 1.00 | 0.05 | −78 | −30 |
| 3 | $Al(i-Bu)_3$ 0.50 | 0.05 | −78 | −30 |
| 4 | $Al(i-Bu)_3$ 0.25 | 0.05 | −78 | −30 |
| 5 | $Al(i-Bu)_3$ 0.15 | 0.05 | −78 | −30 |
| 6 | $Al(i-Bu)_3$ 0.30 | 0.10 | −30 | −37 |
| 7 | $Al(i-Bu)_3$ 0.25 | 0.06 | −60 | −30 |
| 8 | $Al(i-Bu)_3$ 0.25 | 0.06 | −40 | −30 |
| 9 | $Al(i-Bu)_3$ 0.25 | 0.06 | −20 | −30 |
| 10 | $Al(i-Bu)_3$ 0.25 | 0.06 | 0 | −30 |
| 11 | $Al(i-Bu)_3$ 0.25 | 0.06 | −78 | −20 |
| 12 | $Al(i-Bu)_3$ 0.25 | 0.06 | −78 | −10 |
| 13 | $AlEt_3$ 0.50 | 0.20 | −78 | −30 |

TABLE 4 (continued)

| Exp. No. | Polymerization conditions | Alternating copolymer of butadiene and propylene | | | | |
|---|---|---|---|---|---|---|
| | Time (hr.) | Yield (g) | * Intrinsic viscosity [γ] (dl/g) | Microstructure of butadiene unit | | |
| | | | | cis (%) | trans (%) | 1,2 (%) |
| 1 | 16 | 2.62 | 1.02 | — | — | — |
| 2 | 16 | 0.10 | —— | 35 | 57 | 8 |
| 3 | 16 | 0.79 | —— | 28 | 66 | 6 |
| 4 | 16 | 1.25 | —— | 20 | 77 | 3 |
| 5 | 16 | 0.36 | —— | 47 | 50 | 3 |
| 6 | 16 | 1.57 | 2.05 | 18 | 78 | 4 |
| 7 | 16 | 1.46 | 1.50 | — | — | — |
| 8 | 16 | 1.17 | 1.44 | — | — | — |
| 9 | 16 | 1.17 | 1.15 | — | — | — |
| 10 | 16 | 0.98 | 1.99 | — | — | — |
| 11 | 16 | 1.57 | 1.12 | — | — | — |
| 12 | 16 | 1.56 | 1.04 | — | — | — |
| 13 | 16 | 0.33 | 0.70 | | | |

* Measured in chloroform at 30 °C

Example 5.

The usual, dry, air-free technique was employed and 8.0 milliliters toluene and varying amounts of organic titanium compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a low temperature bath at −78°C (it corresponds to catalyst preparation temperature given in Table 5) and varying amounts of triisobutylaluminum solution in toluene (1 molar solution) and a mixture of 2.0 milliliters liquid propylene, 2.0 milliliters liquid butadiene and 2.0 milliliters toluene were put successively into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 5.

TABLE 5

| Exp. No. | Catalysts* | | Catalyst preparation temperature (°C) | Polymerization conditions | |
|---|---|---|---|---|---|
| | Al(i—Bu)$_3$ (mmol) | Organic: titanium compound (mmol) | | Temperature (°C) | Time (hr.) |
| 1 | 0.3 | $TiCl_2(O\overset{\overset{O}{\|}}{C}Et)_2$ | −78 | −30 | 17 |
| 2 | 0.7 | $TiCl_2(O\overset{\overset{O}{\|}}{C}Et)_2$ 0.1 | −78 | −30 | 17 |
| 3 | 0.3 | $O[TiCl(O\overset{\overset{O}{\|}}{C}Et)_2]_2$ 0.05 | −78 | −30 | 17 |
| 4 | 0.7 | $O[TiCl(O\overset{\overset{O}{\|}}{C}Et)_2]_2$ 0.05 | −78 | −30 | 17 |
| 5 | 0.3 | $TiCl(O\overset{\overset{O}{\|}}{C}Et)_2$ | −78 | 20 | 25 |

* $TiCl_2(O\overset{\overset{O}{\|}}{C}Et)_2$: $TiCl_2(O\overset{\overset{O}{\|}}{C}C_2H_5)_2$, $O[TiCl(O\overset{\overset{O}{\|}}{C}Et)_2]_2$: $O[TiCl(O\overset{\overset{O}{\|}}{C}C_2H_5)_2]_2$

TABLE 5 (continued)

| Exp. No. | Alternating copolymer of butadiene and propylene | | | | |
|---|---|---|---|---|---|
| | Yield (g) | Intrinsic** viscosity $[\gamma]$ (dl/g) | Microstructurre of butadiene unit | | |
| | | | cis (%) | trans (%) | 1,2 (%) |
| 1 | 0.37 | — | 18 | 77 | 5 |
| 2 | 0.26 | — | — | — | — |
| 3 | 0.10 | — | 20 | 68 | 12 |
| 4 | 0.09 | — | — | — | — |
| 5 | 0.36 | 0.72 | 32 | 55 | 13 |

** Measured in chloroform at 30 °C.

Example 6.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene, varying amounts of organic titanium compound and varying amounts of halogen compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a low temperature bath at −78°C (it corresponds to catalyst preparation temperature given in Table 6) and varying amounts of organoaluminum compound solution in toluene (1 molar solution) and a mixture of 2.0 milliliters liquid propylene, 2.0 milliliters liquid butadiene and 2.0 milliliters toluene were put successively into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 6.

TABLE 6

| Exp. No. | Catalysts* Organoaluminium compound (mmol) | | Organic titanium compound (mmol) | | Halogen compound (mmol) | | Catalyst preparation temperature (°C) |
|---|---|---|---|---|---|---|---|
| 1 | $Al(i-Bu)_3$ | 0.5 | $TiCl_2(O\overset{O}{\overset{\|}{C}}Et)_2$ | 0.1 | tert-BuCl | 0.1 | −78 |
| 2 | $Al(i-Bu)_3$ | 5.0 | $TiCl(O\overset{O}{\overset{\|}{C}}Et)_3$ | 0.05 | tert-BuCl | 1.0 | −78 |
| 3 | $Al(hexyl)_3$ | 0.5 | $TiCl_3(O\overset{O}{\overset{\|}{C}}Et)$ | 0.2 | $FeCl_3$ | 0.01 | −78 |
| 4 | $Al(i-Bu)_3$ | 2.0 | $TiCl_3(O\overset{O}{\overset{\|}{C}}Et)$ | 0.2 | $MoCl_5$ | 1.0 | −78 |

* $TiCl_2(O\overset{O}{\overset{\|}{C}}Et)_2$: $TiCl_2(O\overset{O}{\overset{\|}{C}}C_2H_5)_2$, tert-BuCl: tert-butyl chloride, $Al(hexyl)_3$: trihexylaluminium.

TABLE 6 (continued)

| Exp. No. | Polymerization conditions Temperature (°C) | Time (hr.) | Alternating copolymer of butadiene and propylene Yield (g) | Microstructure of butadiene unit cis (%) | trans (%) | 1,2 (%) |
|---|---|---|---|---|---|---|
| 1 | 20 | 25 | 0.73 | 23 | 70 | 7 |
| 2 | −40 | 15.5 | 0.19 | 40 | 35 | 25 |
| 3 | −40 | 15.5 | 0.63 | 25 | 70 | 5 |
| 4 | −40 | 15.5 | 0.49 | 18 | 80 | 2 |

Example 7.

The usual, dry, air-free technique was employed and 7.0 milliliters varying amounts of organic titanium compound and varying amounts of halogen compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a constant temperature bath showing predetermined temperature (it corresponds to catalyst preparation temperature given in Table 7) and varying amounts of organoaluminum compound solution in toluene (1 molar solution) were put into the bottles. Thereafter, the bottles were held in a low temperature bath at −78°C and a mixture of 2.0 milliliters liquid propylene, 2.0 milliliters liquid butadiene and 2.0 milliliters toluene was put into the bottles respectively also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 7.

TABLE 7

| Exp. No. | Catalysts* | | | | | | Catalyst preparation temperature (°C) | Polymerization conditions |
|---|---|---|---|---|---|---|---|---|
| | Organoaluminium compound (mmol) | | Organic titanium compound (mmol) | | Halogen compound (mmol) | | | Temperature (°C) |
| 1 | $Al(i-Bu)_3$ | 1.0 | $O[Ti(OAc)_3]_2$ | 0.1 | $AlCl_3.OEt_2$ | 0.1 | −78 | 20 |
| 2 | $Al(i-Bu)_3$ | 0.5 | $O[Ti(OAc)_3]_2$ | 0.1 | $C_6H_5COCl$ | 0.5 | −78 | 20 |
| 3 | $AlEt_3$ | 1.0 | $O[Ti(O\overset{\overset{O}{\Vert}}{C}Et)_3]_2$ | 0.2 | $CrO_2Cl_2$ | 0.5 | 0 | 0 |
| 4 | $Al(i-Bu)_3$ | 1.0 | $O[Ti(O\overset{\overset{O}{\Vert}}{C}Et)_3]_2$ | 0.2 | $AlEt_2Cl$ | 0.5 | −40 | −40 |
| 5 | $Al(i-Bu)_3$ | 2.0 | A | 0.2 | $AlCl_3.OEt_2$ | 0.5 | −78 | 20 |
| 6 | $AlEt_3$ | 2.0 | A | 0.2 | $AlCl_3.OEt_2$ | 0.5 | −78 | 20 |

* $O[Ti(OAc)_3]_2$: $O[Ti(O\overset{\overset{O}{\Vert}}{C}CH_3)_3]_2$, $O[Ti(O\overset{\overset{O}{\Vert}}{C}Et)_3]_2$: $O[Ti(O\overset{\overset{O}{\Vert}}{C}C_2H_5)_3]_2$, A:

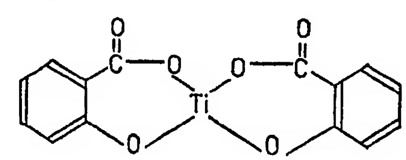


TABLE 7 (continued)

| Exp. No. | Polymerization conditions | Alternating copolymer of butadiene and propylene | | | | |
|---|---|---|---|---|---|---|
| | Time (hr.) | Yield (g) | ** Intrinsic viscosity [γ] (dl/g) | Microstructure of butadiene unit | | |
| | | | | cis (%) | trans (%) | 1,2 (%) |
| 1 | 22 | 1.66 | 0.6 | 26 | 63 | 11 |
| 2 | 22 | 0.15 | — | 22 | 65 | 13 |
| 3 | 91 | 0.01 | — | — | — | — |
| 4 | 28.5 | 0.20 | — | 25 | 57 | 8 |
| 5 | 48 | 0.05 | — | 18 | 54 | 28 |
| 6 | 48 | 0.11 | — | 10 | 67 | 24 |

** Measured in chloroform at 30 °C.

Example 8.

The usual, dry, air-free technique was employed and 8.0 milliliters toluene and varying amounts of organic titanium compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a low temperature bath at −20°C (it corresponds to catalyst preparation temperature shown in Table 8) and 1.00 milliliter triisobutylaluminum solution in toluene (1 molar solution) was put into the bottles respectively. Thereafter, the bottles were held in a low temperature bath at −78°C and varying amounts of liquid propylene and varying amounts of liquid butadiene were put successively into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature for 16 hours. The results were summarized in Table 8.

TABLE 8

| Exp. No. | Catalyst | | Catalyst preparation temperature (°C) | Monomers | | Polymerization condition |
|---|---|---|---|---|---|---|
| | $Al(i-Bu)_3$ (mmol) | Organic:titanium compound, $TiCl_3OC(=O)C_6H_5$ (mmol) | | Liquid propylene (ml) | Liquid butadiene (ml) | Temperature (°C) |
| 1 | 1.00 | 0.41 | −20 | 4.0 | 0.4 | 0 |
| 2 | 1.00 | 0.41 | −20 | 4.0 | 0.8 | 0 |
| 3 | 1.00 | 0.41 | −20 | 4.0 | 0.4 | −40 |
| 4 | 1.00 | 0.41 | −20 | 4.0 | 0.8 | −40 |
| 5 | 1.00 | 0.44 | −20 | 2.0 | 2.0 | −40 |
| 6 | 1.00 | 0.44 | −20 | 2.5 | 2.0 | −40 |
| 7 | 1.00 | 0.44 | −20 | 3.0 | 2.0 | −40 |
| 8 | 1.00 | 0.44 | −20 | 4.0 | 2.0 | −40 |
| 9 | 1.00 | 0.44 | −20 | 5.0 | 2.0 | −40 |

TABLE 8 (continued)

| Exp. No. | Polymerization conditions | Alternating copolymer of butadiene and propylene | | | | |
|---|---|---|---|---|---|---|
| | Time (hr.) | Yield (g) | * Intrinsic viscosity [η] (dl/g) | Microstructure of butadiene unit | | |
| | | | | cis (%) | trans (%) | 1,2 (%) |
| 1 | 16 | 0.69 | — | 17 | 80 | 3 |
| 2 | 16 | 1.05 | 0.66 | 16 | 79 | 5 |
| 3 | 16 | 0.43 | 0.88 | 4 | 96 | 0 |
| 4 | 16 | 0.15 | 1.25 | 6 | 93 | 1 |
| 5 | 16 | 1.89 | 4.84 | — | — | — |
| 6 | 16 | 1.67 | 4.00 | 13 | 85 | 2 |
| 7 | 16 | 0.86 | 3.40 | — | — | — |
| 8 | 16 | 0.86 | 3.10 | 10 | 88 | 2 |
| 9 | 16 | 0.26 | 2.84 | 12 | 86 | 2 |

* Measured in chloroform at 30°C.

Example 9.

The usual, dry, air-free technique was employed and 0.06 millimole

$$TiCl_3O\overset{O}{\overset{\|}{C}}CH_3$$

was put into a 25 milliliter glass bottle at 20°C. Then, the bottle was held in a low temperature bath at −78°C and 0.25 milliliter triisobutylaluminum solution in toluene (1 molar solution), 10.0 milliliters liquid propylene and 2.0 milliliters liquid butadiene were put successively into the bottle also employing the usual, dry, air-free technique. Thereafter, the bottle was sealed and the contents allowed to copolymerize at −30°C for 16 hours. The yield of the alternating copolymer of butadiene and propylene was 0.73g. Intrinsic viscosity of the copolymer was 0.92 (dl/g).

Example 10.

The usual, dry, air-free technique was employed and 8.0 milliliters toluene and 0.06 millimole

$$TiCl_3O\overset{\overset{\large O}{\|}}{C}C_6H_5$$

were put into a 25 milliliter glass bottle at 20°C. Then, the bottle was held in a low temperature bath at −78°C and 0.60 milliliter triisobutylaluminum solution in toluene (1 molar solution), 1.0 milliliter liquid butadiene and 5.0 milliliters liquid propylene were put successively into the bottle also employing the usual, dry, air-free technique. Thereafter, the bottle was sealed and the contents allowed to copolymerize at 40°C for 1.5 hours. The yield of the alternating copolymer was 0.06g.

Example 11.

The usual, dry, air-free technique was employed and 8.0 milliliters toluene, 0.15 millimole

$$TiCl_3O\overset{\overset{\large O}{\|}}{C}C_6H_5,$$

2.0 milliliters liquid butadiene, 2.0 milliliters liquid propylene and 0.5 milliliter triisobutylaluminum solution in toluene (1 molar solution) were put successively into a 25 milliliter glass bottle at −30°C. Then, the bottle was sealed and the contents allowed to copolymerize at −40°C for 15.5 hours. The yield of the alternating copolymer was 1.63. The microstructure of butadiene unit of the copolymer was as follows: cis; 2%, trans; 95%, 1,2; 3%.

Example 12.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene, 0.2 millimole

$$O[Ti(O\overset{\overset{\large O}{\|}}{C}CH_3)_3]_2,$$

2.0 milliliters triisobutylaluminum solution in toluene (1 molar solution) and 0.5 millimole $AlCl_3.O(C_2H_5)_2$ were put successively into a 25 milliliter glass bottle at −40°C. Then, the bottle was held in a low temperature bath at −78°C and a mixture of 2.0 milliliters liquid propylene, 2.0 milliliters liquid butadiene and 2.0 milliliters toluene was put into the bottle also employing the usual, dry, air-free technique. Thereafter, the bottle was sealed and the contents allowed to copolymerize at −40°C for 18 hours. The yield of the MEK soluble alternating copolymer of butadiene and propylene was 0.10g and that of the MEK insoluble, diethyl ether soluble fraction was 0.09g. The microstructure of butadiene unit of the latter fraction was as follows: cis; 20%, trans; 65%, 1,2; 15%.

Example 13.

The usual, dry, air-free technique was employed and 10.0 milliliters toluene, 0.05 milliliter tert-butylchloride solution in toluene (1 molar solution) and 0.4 milliliter triisobutylaluminum solution in toluene (1 molar solution) were put into a 25 milliliter glass bottle at 25°C. Then the bottle was held in a low temperature bath at −32°C and 0.12 millimole

$$TiCl_3O\overset{\overset{\large O}{\|}}{C}CH_3$$

was put into the bottle. Thereafter, the bottle was held in a low temperature bath at −78°C and a mixture of 2.0 milliliters liquid propylene, 2.0 milliliters liquid butadiene and 2.0 milliliters toluene was put into the bottle also employing the usual, dry, air-free technique. Then, the bottle was sealed and the contents allowed to copolymerize at −40°C for 16 hours. The yield of the alternating copolymer of butadiene and propylene was 1.37g and its intrinsic viscosity was 2.8 (dl/g) in toluene at 30°C. By using the two components catalyst system of 0.4 millimole triisobutylaluminum and 0.12 millimole

$$TiCl_3O\overset{\overset{\large O}{\|}}{C}CH_3,$$

butadiene and propylene alternating copolymerization reaction was carried out. The yield of the alternating copolymer was 1.18g and its intrinsic viscosity was 2.65 (dl/g) in toluene at 30°C. From these experiments, the effect obtained by the addition of halogen compound can be found.

Example 14.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene and varying amounts of organic titanium compound were put into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a constant temperature bath showing predetermined temperature (it corresponds to catalyst preparation temperature given in Table 9) and varying amounts of organoaluminum compound solution in toluene (1 molar solution) was put into the bottles respectively. Thereafter, the bottles were held in a low temperature bath at −78°C and varying amounts of liquid α-olefin and 2.0 milliliters liquid butadiene were put successively into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 9.

TABLE 9

| Exp. No. | Catalysts | | | | Catalyst preparation temperature | Monomers* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Organoaluminum compound (mmol) | | Organic:titanium compound (mmol) | | | Liquid-olefin (ml) | | Liquid butadiene (ml) | |
| 1 | $Al(i-Bu)_3$ | 0.5 | $TiCl_3OC(=O)CH_3$ | 0.1 | −78 | styrene | 3.0 | BD | 2.0 |
| 2 | $Al(i-Bu)_3$ | 0.5 | $TiCl_3OC(=O)CH_3$ | 0.1 | −78 | butene-1 | 2.0 | BD | 2.0 |
| 3 | $Al(i-Bu)_3$ | 0.6 | $TiCl_3OC(=O)C_6H_5$ | 0.06 | −40 | 4-M-P-1 | 2.0 | BD | 2.0 |
| 4 | $Al(hexyl)_3$ | 0.5 | $TiCl_2(OC(=O)Et)_2$ | 0.2 | 0 | hexene-1 | 6.0 | BD | 1.0 |

* 4-M-P-1: 4-methyl-penten-1, BD: butadiene

TABLE 9 (continued)

| Exp. No. | Polymerization condition | | Alternating copolymer of butadiene and α-olefin | |
|---|---|---|---|---|
| | Temperature (°C) | Time (hr.) | Yield (g) | Intrinsic viscosity ** [γ] (dl/g) |
| 1 | −30 | 21 | 0.14 | — |
| 2 | −30 | 16 | 1.38 | 1.28 |
| 3 | −40 | 21 | 0.18 | — |
| 4 | 40 | 1/6 | 0.61 | 0.8 |

** Measured in chloroform at 30 °C.

Example 15.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene, 0.2 millimole organic titanium compound and varying amounts of halogen compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a constant temperature bath showing given predetermined temperature (it corresponds to catalyst preparation temperature given in Table 10) and varying amounts of organo-aluminum compound solution in toluene (1 molar solution) were put into the bottles respectively. Thereafter, the bottles were held in a low temperature bath at −78°C and varying amounts of liquid α-olefin and 2.0 milliliters liquid butadiene were put successively into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 10.

TABLE 10

| Exp. | Catalysts | | | | | | Catalyst preparation temperature (°C) |
|---|---|---|---|---|---|---|---|
| | Organoaluminum compound (mmol) | | Organic:titanium compound (mmol) | | Halogen compound (mmol) | | |
| 1 | $Al(hexyl)_3$ | 2.0 | $O[Ti(OAc)_3]_2$ | 0.2 | $MoCl_5$ | 0.2 | −40 |
| 2 | $AlEt_3$ | 5.0 | $O[Ti(OAc)_3]_2$ | 0.2 | $FeCl_3$ | 1.0 | −78 |
| 3 | $Al(hexyl)_3$ | 1.0 | $TiCl_2(\overset{\overset{\displaystyle O}{\|}}{C}OEt)_2$ | 0.2 | $AlEtCl_2$ | 0.3 | −78 |

TABLE 10 (continued)

| Exp. No. | Monomers* | | | | Polymerization conditions | | Yield of alternating copolymer of butadiene and α-olefin (g) |
|---|---|---|---|---|---|---|---|
| | Liquid α-olefin (ml) | | Liquid butadiene (ml) | | Temperature (°C) | Time (hr.) | |
| 1 | butene-1 | 2.0 | BD | 2.0 | −40 | 43 | 0.04 |
| 2 | pentene-1 | 5.0 | BD | 2.0 | 0 | 19 | 0.18 |
| 3 | hexene-1 | 2.0 | BD | 2.0 | −40 | 21 | 0.05 |

* BD: butadiene

Example 16.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene and varying amounts of organic titanium compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a low temperature bath at −78°C (it corresponds to catalyst preparation temperature given in Table 11) and varying amounts of triisobutylaluminum solution in toluene (1 molar solution), 2.0 milliliters liquid butadiene and varying amounts of liquid α-olefin were put successively into the bottles also employing the usual, dry, air-free technique. Thereafter, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 11.

TABLE 11

| Exp. No. | Catalysts | | | Catalyst preparation temperature (°C) | Monomers* | | | |
|---|---|---|---|---|---|---|---|---|
| | $Al(i-Bu)_3$ (mmol) | Organic: titanium compound (mmol) | | | Liquid α-olefin (ml) | | Liquid butadiene (ml) | |
| 1 | 1.0 | $TiCl(OC(=O)Et)_3$ | 0.2 | −78 | butene-1 | 4.0 | BD | 2.0 |
| 2 | 0.5 | $TiCl_3(OC(=O)CH_3)$ | 0.02 | −78 | pentene-1 | 2.8 | BD | 2.0 |
| 3 | 0.5 | $TiCl_3(OC(=O)CH_3)$ | 0.1 | −78 | pentene-1 | 2.8 | BD | 2.0 |

* BD: butadiene

TABLE 11 (continued)

| Exp. No. | Polymerization conditions | | Yield of alternating copolymer of butadiene and $\alpha$-olefin (g) |
|---|---|---|---|
| | Temperature (°C) | Time (hr.) | |
| 1 | 0 | 21 | 0.18 |
| 2 | −30 | 16 | 0.03 |
| 3 | −30 | 16 | 1.80 |

Example 17.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene, 0.2 millimole organic titanium compound and varying amounts of halogen compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a constant temperature bath showing a predetermined temperature (it corresponds to catalyst preparation temperature) and 1.0 milliliter organoaluminum compound solution in toluene (1 molar solution) was put into the bottles respectively. Thereafter, the bottles were held in a low temperature bath at −78°C and 2.0 milliliters liquid butadiene and varying amounts of liquid $\alpha$-olefin were put successively into the bottles also employing the usual, dry air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature for 21 hours. The results were summarized in Table 12.

TABLE 12

| Exp. No. | Catalysts | | | | | | Catalyst preparation temperature (°C) | Monomers | |
|---|---|---|---|---|---|---|---|---|---|
| | Organoaluminum compound (mmol) | | Organic:titanium compound (mmol) | | Halogen compound (mmol) | | | Liquid α-olefin (ml) | |
| 1 | $Al(i-Bu)_3$ | 1.0 | $TiCl(OC(=O)Et)_2$ | 0.2 | $CrO_2Cl_2$ | 0.2 | −78 | butene-1 | 4.0 |
| 2 | $AlEt_3$ | 1.0 | $O[TiCl(OC(=O)Et)_2]_2$ | 0.2 | $AlCl_3 \cdot OEt_2$ | 0.01 | −40 | butene-1 | 2.0 |
| 3 | $AlEt_3$ | 1.0 | $TiCl_3(OC(=O)C_6H_5)$ | 0.06 | $I_2$ | 0.2 | −40 | pentene-1 | 2.0 |

TABLE 12 (continued)

| Exp. No. | Monomers* | | Polymerization conditions | | Alternating copolymer of butadiene and α-olefin | |
|---|---|---|---|---|---|---|
| | Liquid butadiene (ml) | | Temperature (°C) | Time (hr) | Yield (g) | Intrinsic** viscosity [γ] (dl/g) |
| 1 | BD | 2.0 | 0 | 21 | 0.26 | — |
| 2 | BD | 2.0 | 0 | 21 | 0.34 | 0.82 |
| 3 | BD | 2.0 | −40 | 21 | 0.21 | — |

* BD: butadiene, ** Measured in chloroform at 30°C.

### Example 18.

The usual, dry, air-free technique was employed and 4.0 milliliters toluene and 0.2 millimole

$$TiCl_3O\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

were put into a 25 milliliter glass bottle at 20°C. Then the bottle was held in a low temperature bath at −78°C and 1.0 milliliter triisobutylaluminum solution in toluene (1 molar solution) and 6.0 milliliters liquid B—B fraction were put successively into the bottle also employing the usual, dry, air-free technique. Thereafter, the bottle was sealed and the contents allowed to copolymerize at −30°C for 24 hours. The yield of alternating copolymer of butadiene and butene-1 was 0.55g.

The molar composition of the B—B fraction used was as follows:

| | |
|---|---|
| propane | 0.03 mole % |
| propylene | 0.05 ,, |
| methylacetylene | 0.69 ,, |
| isobutane | 0.52 ,, |
| n-butane | 3.67 ,, |
| isobutylene | 26.22 ,, |
| butene-1 | 14.18 ,, |
| trans-butene-2 | 5.18 ,, |
| cis-butene-2 | 4.12 ,, |
| 1,3-butadiene | 44.02 ,, |
| 1,2-butadiene | 0.52 ,, |
| ethyl acetylene | 0.16 ,, |
| vinyl acetylene | 0.64 ,, |

### Example 19.

5.91 Kg alternating copolymer of butadiene and propylene was prepared from 8.10 Kg propylene and 8.50 Kg butadiene at −40°C for 17.5 hours. The catalyst used was prepared from 1.11 mole tributylaluminum and 0.44 mole

$$TiCl_3O\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5$$

at −20°C. The number average molecular weight of the copolymer was 93,500.

The vulcanization was carried out in the following way:

| | |
|---|---|
| 100 | parts of the above copolymer, |
| 50 | parts of oil furnace black (HAF), |
| 5 | parts of zinc oxide, |
| 1.5 | parts of sulphur, |
| 1 | part of stearic acid, |
| 1 | part of phenyl-β-naphthyl amine and |
| 1 | part of benzothiazyl disulfide |

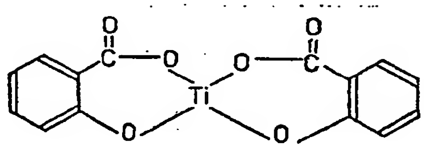
were mixed on a roller and vulcanized at 150°C for 20 minutes.

The product obtained by the vulcanization had the following values:

| | | |
|---|---|---|
| elongation at break at 25°C | : | 390% |
| tensile strength at 25°C | : | 226 Kg/cm² |
| modulus 300% at 25°C | : | 156 Kg/cm² |

### Example 20.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene, 0.2 millimole



and 0.5 millimole stannic chloride were put successively into a 25 milliliter glass bottle at 20°C. Then, the bottle was held in a low temperature bath at −40°C and 1.0 milliliter triethylaluminum solution in toluene (1 molar solution) was put into the bottle. Thereafter, the bottle was held in a low temperature bath at −78°C and 4.0 milliliters liquid pentene-1 and 2.0 milliliters liquid butadiene were put successively into the bottle also employing the usual, dry, air-free technique. Then, the bottle was sealed and the contents allowed to copolymerize at 20°C for 48 hours. MEK soluble alternating copolymer of butadiene and pentene-1 was obtained. It's yield was 0.40g.

### Example 21.

The usual, dry, air-free technique was employed and 8.0 milliliters toluene and varying amounts of organic titanium compound were put into 25 milliliter glass bottles at 25°C. Then, the bottles were held in a constant temperature bath showing predetermined temperature (it corresponds to catalyst preparation temperature) and varying amounts of organoaluminum compound solution in toluene (1 molar solution) were put into the bottles respectively. Thereafter, the bottles were held in a low temperature bath at −78°C and a mixture of 2.0 milliliters liquid propylene and 2.0 milliliters liquid isoprene was put into the each bottle also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 13.

 26

TABLE 13

| Exp. No. | Catalyst: Organoaluminum compound (mmole) | | Catalyst: Organic:titanium compound (mmole) | | Catalyst preparation temperature (°C) | Polymerization conditions: Temperature (°C) | Polymerization conditions: Time (hr.) |
|---|---|---|---|---|---|---|---|
| 1 | $Al(i-Bu)_3$ | 1.0 | $TiCl_3(O\overset{O}{\overset{\|}{C}}CH_3)$ | 0.2 | −40 | −40 | 18 |
| 2 | $Al(i-Bu)_3$ | 1.0 | $TiCl_2[O\overset{O}{\overset{\|}{C}}CH(CH_3)CH_3]_2$ | 0.2 | −40 | −40 | 18 |
| 2 | $Al(i-Bu)_3$ | 1.0 | $TiCl_3(O\overset{O}{\overset{\|}{C}}C_6H_5)$ | 0.5 | −40 | −40 | 18 |
| 4 | $Al(i-Bu)_3$ | 1.0 | $O[TiCl_2(OCC_6H_5)]_2$ | 0.25 | −40 | −40 | 18 |
| 5** | $AlEt_3$ | 0.3 | $TiCl_3O\overset{O}{\overset{\|}{C}}C_6H_5$ | 0.1 | −78 | 20 | 145 |

** Microstructure of isoprene unit of the alternating copolymer is as follows: 1,2:0%, 1,4:90%, 3,4:10%

TABLE 13 (continued)

| Exp. No. | Alternating copolymer of isoprene and propylene | |
|---|---|---|
| | Yield (g) | *Intrinsic viscosity [γ] (dl/g) |
| 1 | 0.30 | — |
| 2 | 0.13 | — |
| 3 | 1.40 | — |
| 4 | 0.43 | — |
| 5** | 0.97 | 0.40 |

* Measured in chloroform at 30°C.

The following results support the conclusion that the copolymer is an alternating copolymer of isoprene and propylene.

1) In the infra-red spectrum of the copolymer (Fig. 1), there can be seen no peak near 909 $cm^{-1}$ which corresponds to the band assigned to 1,2-structure of polyisoprene. The 890 $cm^{-1}$ band is assigned to 3,4-structure of isoprene unit and the broad band at 850 $cm^{-1}$ is assigned to 1,4-structure of isoprene unit of the copolymer. Therefore, it is concluded that microstructure of isoprene unit of the copolymer is substantially composed of 3,4- and 1,4- structures.

2) In Fig. 2, the triplet at 4.8τ is ascribed to the proton directly attached to the double bond of 1,4-structure isoprene unit and the weak doublet at 5.3τ is ascribed to isopropenyl methylene group of 3,4-isoprene unit of the copolymer. Measuring the ratio of peak area of the triplet at 4.8τ to half of that of the peak at 5.3τ, the ratio of 1,4-structure to 3,4-structure is found to be 94/6.

3) Copolymer composition were determined by measuring the ratio of peak area of the triplet at 4.8τ and half of the peak area of the doublet at 5.3τ to one third of the peak area of the doublet at 9.2τ assigned to methyl group of propylene unit of the copolymer. It is found that the composition of the copolymer according to the NMR analysis substantially agrees well with the calculated value for the 1:1 copolymer of isoprene and propylene.

4) 1,4-polyisoprene shows a peak at 7.95τ which is assigned to methylene group of the polymer. On the other hand, there can be seen substantially no peak at 7.95τ in the NMR spectrum of the copolymer obtained in this example. This means that there are substantially no 1,4-isoprene repeating units in the copolymer.

8.1τ peak may be assigned to methylene group of 1,4-isoprene unit of the alternating copolymer.

5) The copolymerization reaction gives 1:1 copolymer over a wide range of initial monomer composition.

6) The copolymerization reaction gives 1:1 copolymer independently of polymerization time.

In Fig. 2, 8.32τ peak may be ascribed to methyl group of cis-1,4-structure of isoprene unit and 8.42τ peak may also be ascribed to the total of methyl groups of trans-1,4- and 3,4-structures of isoprene unit of the copolymer. Therefore, it is concluded that the structure of isoprene unit of the copolymer is mainly cis-1,4-structure.

In Fig. 11, in contrast to the spectrum in Fig. 1, a sharp peak appears at 909 $cm^{-1}$. The band is assigned to 1,2-structure of isoprene unit of the alternating copolymer. The strength of the broad 850 $cm^{-1}$ band assigned to 1,4-structure of isoprene unit in Fig. 1 is stronger than that of the one in Fig. 11. In Fig. 12, in contrast with the spectrum in Fig. 2, it is found that most of the 1,4-structure units of isoprene is trans-1,4-structure.

From the above results, it is clear that the structure of the alternating copolymer of isoprene and propylene prepared by the method of this invention is quite different from that of the one prepared by the organoaluminum compound-vanadium compound type catalyst system. The alternating copolymer of the present invention is a novel material.

From Figs. 11 and 12, it is also found that microstructure of isoprene unit of the alternating copolymer is as follows:

| | | |
|---|---|---|
| 1,4-structure | : | 88% |
| 1,2-structure | : | 5% |
| 3,4-structure | : | 7% |

The special feature of the structure of alternating copolymer of isoprene and propylene prepared by the method of this invention is as follows:

a. Microstructure of isoprene unit of the alternating copolymer is composed of large amounts of 1,4-structure and minor amounts of 3,4-structure.

b. The most part of the 1,4-structure units of isoprene is cis-1,4-structure.

c. Existence of 1,2-structure unit of isoprene can scarcely be detected by its infra-red spectrum.

Example 22.

The usual, dry, air-free technique was employed and 8.0 milliliters toluene, varying amounts of organic titanium compound and varying amounts of halogen compound were put into 25 milliliter glass bottles at 25°C. Then, the bottles were held in a constant temperature bath showing predetermined temperature (it corresponds to catalyst preparation temperature given in Table 14) and varying amounts of triisobutylaluminum solution in toluene (1 molar solution) were put into the bottles respectively. Thereafter, the bottles were held in a low temperature bath at −78°C and a mixture of 2.0 milliliters liquid propylene and 2.0 milliliters liquid isoprene was put into each bottle also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature and for predetermined time. The results were summarized in Table 14.

TABLE 14

| Exp. No. | Catalysts* | | |
|---|---|---|---|
| | $Al(i-Bu)_3$ (mmole) | Organictitanium compound (mmol) | Halogen or halogen compound (mmole) |
| 1 | 1.0 | $TiCl_3(O\overset{\overset{O}{\|}}{C}CH_3)$ 0.2 | $C_6H_5COCl$ 0.1 |
| 2 | 1.0 | $TiCl_2[O\overset{\overset{O}{\|}}{C}CH(CH_3)CH_3]_2$ 0.2 | $AlCl_3.OEt_2$ 0.1 |
| 3 | 1.0 | $TiCl_2[O\overset{\overset{O}{\|}}{C}CH(CH_3)CH_3]_2$ 0.2 | tert-BuCl 0.2 |
| 4 | 1.0 | $TiCl_2[O\overset{\overset{O}{\|}}{C}CH(CH_3)CH_3]_2$ 0.2 | $I_2$ 0.1 |
| 5 | 1.0 | $O[TiCl_2(O\overset{\overset{O}{\|}}{C}C_6H_5)]_2$ 0.25 | $SnCl_4$ 0.1 |
| 6 | 1.0 | $O[Ti(O\overset{\overset{O}{\|}}{C}CH_3)_3]_2$ 0.1 | $SnCl_4$ 0.2 |
| 7 | 1.0 | $O[Ti(O\overset{\overset{O}{\|}}{C}CH_3)_3]_2$ 0.1 | $AlEtCl_2$ 0.2 |
| 8 | 1.0 | $O[Ti(OCCH_3)_3]_2$ 0.1 | $FeCl_3$ 0.1 |
| 9 | 1.0 | $Ti(Oi\text{-}Pr)_2(O\overset{\overset{O}{\|}}{C}CH_3)_2$ 0.2 | $SbCl_5$ 0.2 |
| 10 | 1.0 | $Ti(Oi\text{-}Pr)_2(O\overset{\overset{O}{\|}}{C}CH_3)_2$ 0.2 | $VOCl_3$ 0.1 |
| 11 | 0.3 | $O[Ti(O\overset{\overset{O}{\|}}{C}CH_3)_3]_2$ 0.1 | $Br_2$ 0.1 |

* $Ti(Oi\text{-}Pr)_2(O\overset{\overset{O}{\|}}{C}CH_3)_2$ : $Ti[OCH(CH_3)CH_3]_2(O\overset{\overset{O}{\|}}{C}CH_3)_2$

TABLE 14 (continued)

| Exp. No. | Catalyst preparation temperature (°C) | Polymerization conditions | | Yield of alternating copolymer of isoprene and propylene (g) |
|---|---|---|---|---|
| | | Temperature (°C) | Time (hr.) | |
| 1 | −40 | −40 | 18 | 0.48 |
| 2 | −40 | −40 | 18 | 0.33 |
| 3 | −40 | −40 | 18 | 0.20 |
| 4 | −40 | −40 | 18 | 0.16 |
| 5 | −40 | −40 | 18 | 0.62 |
| 6 | −40 | −40 | 18 | 0.02 |
| 7 | −40 | −40 | 18 | 0.04 |
| 8 | −40 | −40 | 18 | 0.02 |
| 9 | −40 | −40 | 18 | 0.02 |
| 10 | −40 | −40 | 18 | 1.57 |
| 11 | −78 | 20 | 94 | 0.34 |

Example 23.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene and 0.21 millimole organic titanium compound were put into 25 milliliter glass bottles at 25°C. Then, the bottles were held in a constant temperature bath showing predetermined temperature (it corresponds to catalyst preparation temperature given in Table 15) and 0.50 milliliter triisobutylaluminum solution in toluene (1 molar solution) were put into the bottles respectively. Thereafter, the bottles were held in a low temperature bath at −78°C and a mixture of 2.0 milliliters liquid propylene and 2.0 milliliters liquid isoprene was put into each bottle also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at predetermined temperature for predetermined time. The results were summarized in Table 15.

TABLE 15

| Exp. No. | Catalysts | | Catalyst preparation temperature (°C) | Polymerization conditions | | Alternating copolymer of isoprene and propylene | |
|---|---|---|---|---|---|---|---|
| | $Al(i-Bu)_3$ (mmole) | $TiCl_3(OC(=O)C_6H_5)$ (mmole) | | Temperature (°C) | Time (hr.) | Yield (g) | Intrinsic viscosity,* [γ] (di/g) |
| 1 | 0.50 | 0.21 | −78 | −40 | 16 | 0.24 | 0.50 |
| 2 | 0.50 | 0.21 | −50 | −40 | 16 | 0.29 | 0.80 |
| 3 | 0.50 | 0.21 | −30 | −40 | 16 | 0.47 | 1.00 |
| 4 | 0.50 | 0.21 | −20 | −40 | 16 | 0.54 | 1.30 |
| 5 | 0.50 | 0.21 | 0 | −40 | 16 | 0.51 | 1.32 |
| 6 | 0.50 | 0.21 | 20 | −40 | 16 | 0.06 | — |
| 7 | 0.50 | 0.21 | −20 | −20 | 20 | 0.71 | 0.67 |
| 8 | 0.50 | 0.21 | −20 | 0 | 20 | 0.59 | 0.60 |
| 9 | 0.50 | 0.21 | 0 | −20 | 20 | 0.62 | — |
| 10 | 0.50 | 0.21 | 0 | 0 | 20 | 0.58 | — |

* Measured in chloroform at 30°C.

3.0 Kg alternating copolymer prepared under the same polymerization conditions as Exp. No. 4 was vulcanized as follows:

100 parts of copolymer,
50 parts of oil furnace black (H.A.F.),
5 parts of zinc oxide,
1.5 parts of sulphur,
1 part of stearic acid,
1 part of phenyl-β-naphthylamine and
1 part of benzothiazyl disulfide

were mixed on a roller and vulcanized at 140°C for 30 minutes. The product obtained by the vulcanization had the following values:

| | | |
|---|---|---|
| elongation at break at 25°C | : | 510% |
| tensile strength at 25°C | : | 169 $Kg/cm^2$ |
| modulus 300% at 25°C | : | 102 $Kg/cm^2$ |

## Example 24.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene, 0.1 millimole

$$O[Ti(O\overset{\overset{\displaystyle O}{\|}}{C}CH_3)_3]_2$$

and 0.3 milliliter ethylaluminum dichloride solution in toluene (1 molar solution) were put successively into a 25 milliliter glass bottle at 20°C. Then, the bottle was held in a low temperature bath at −78°C and 1.0 milliliter triisobutylaluminum solution in toluene (1 molar solution) and a mixture of 3.0 milliliters liquid hexene-1 and 2.0 milliliters liquid isoprene were put successively into the bottle also employing the usual, dry, air-free technique. Thereafter, the bottle was sealed and allowed to copolymerize at −30°C for 16 hours. The yield of the alternating copolymer of isoprene and hexene-1 was 0.23 g. The microstructure of isoprene unit of the copolymer was as follows:

1,2: 0%, 1,4: 92%, 3,4: 8%

The following results support the conclusion that the copolymer is an alternating copolymer of isoprene and hexene-1.

1) In the infra-red spectrum of the copolymer (Fig. 7), there can be seen no peak near 909 $cm^{-1}$. Therefore, it is concluded that microstructure of isoprene unit of the alternating copolymer is substantially composed of 3,4- and 1,4-structures.
2) In Fig. 8, measuring the ratio of peak area of the triplet at 4.8τ to half of that of the weak peak at 5.3τ, the ratio of 1,4-structure to 3,4-structure is found to be 90/10.
3) It is found that the composition of the copolymer according to the NMR analysis substantially agrees well with the calculated value for the 1:1 copolymer of isoprene and hexene-1. The method for measuring the copolymer compositions was applied as was used in the case of alternating copolymer of isoprene and butene-1.
4) In Fig. 8, there can be seen substantially no peak at 7.95τ corresponding to 1,4-isoprene repeating unit. This means that 1,4-isoprene repeating unit does not appear in the copolymer.
5) The copolymerization reaction gives 1:1 copolymer over a wide range of initial monomer composition.
6) The copolymerization reaction gives 1:1 copolymer independently of polymerization time.

In Fig. 8, as in the case of alternating copolymer of isoprene and propylene, by comparing peak area of 8.35τ peak and that of 8.40τ shoulder, it is found that the structure of isoprene unit of the copolymer is mainly cis-1,4-structure.

The alternating copolymer of isoprene and hexene-1 is also found to be a new material.

## Example 25.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene, 0.2 millimole organic titanium compound and 0.5 millimole halogen compound were put successively into 25 milliliter glass bottles at 20°C. Then, the bottles were held in a constant temperature bath showing predetermined temperature (it corresponds to catalyst preparation temperature given in Table 16) and 2.0 milliliters organoaluminum compound solution in toluene (1 molar solution) was put into each bottle. Thereafter, the bottles were held in a low temperature bath at −78°C and 2.0 milliliters liquid isoprene and 3.0 milliliters liquid α-olefin were put successively into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at −40°C for 28.5 hours. The results were summarized in Table 16.

TABLE 16

| Exp. No. | Catalysts: Organoaluminum compound (mmole) | Catalysts: Organic-titanium compound (mmole) | Catalysts: Halogen compound (mmole) | Catalyst preparation temperature (°C) |
|---|---|---|---|---|
| 1 | $Al(i-Bu)_3$ 2.0 | $O[Ti(\overset{O}{\overset{\Vert}{C}}OEt)_3]_2$ 0.2 | $AlCl_3.OEt_2$ 0.5 | −40 |
| 2 | $Al\,Et_3$ 2.0 | $O[Ti(\overset{O}{\overset{\Vert}{C}}OEt)_3]_2$ 0.2 | $AlEtCl_2$ 0.5 | −78 |

TABLE 16 (continued)

| Exp. No. | Monomers | | Polymerization conditions | | Alternating copolymer of isoprene and α-olefin | | | |
|---|---|---|---|---|---|---|---|---|
| | Liquid α-olefin (ml) | Liquid isoprene (ml) | Temperature (°C) | Time (hr.) | Yield (g) | Microstructure of isoprene unit: 1,2 (%) | 1,4 (%) | 3,4 (%) |
| 1 | pentene-1 3.0 | 2.0 | −40 | 28.5 | 0.99 | 0 | 94 | 6 |
| 2 | butene-1 3.0 | 2.0 | −40 | 28.5 | 0.19 | 0 | 93 | 7 |

The following results support the conclusion that the copolymer obtained in Experiment 2 of Example 25 is an alternating copolymer of isoprene and butene-1.

1) In the infra-red spectrum of the copolymer (Fig. 3), there can be seen no peak near 909 $cm^{-1}$ which corresponds to the band assigned to 1,2-structure of polyisoprene. The 890 $cm^{-1}$ and 845 $cm^{-1}$ bands are assigned to 3,4- and 1,4-structure of isoprene unit of the copolymer, respectively. Therefore, it is concluded that microstructure of isoprene unit of the copolymer is substantially composed of 3,4- and 1,4-structures.

2) In Fig. 4, the triplet at 4.8$\tau$ is ascribed to the proton directly attached to 1,4-isoprene double bond and the weak peak at 5.3$\tau$ is ascribed to isopropenyl methylene group of 3,4-isoprene unit of the copolymer. Measuring the ratio of peak area of the triplet at 4.8$\tau$ to half of that of the peak at 5.3$\tau$, the ratio of 1,4-structure to 3,4-structure is found to be 93/7.

3) Copolymer composition were determined as follows:

if A is peak area of the triplet at 4.8$\tau$,
B is peak area of the peak at 5.3$\tau$ and
C is peak area of all peaks appearing in the region from 7.5$\tau$ to 9.5$\tau$,

the molar ratio of isoprene to butene-1 in the copolymer can be shown by the following equation;

$$\frac{\text{isoprene}}{\text{butene-1}} = \frac{A+\frac{B}{2}}{\{C-(7A+3B)\}1/8}$$

It is found that the composition of the copolymer according to the NMR analysis substantially agrees well with the calculated value for the 1:1 copolymer of isoprene and butene-1.

4) In fig. 4, there can be seen substantially no peak at 7.95$\tau$ corresponding to 1,4-isoprene repeating unit. This means that 1,4-isoprene repeating unit does not appear in the copolymer.

5) The copolymerization reaction gives 1:1 copolymer over a wide range of initial monomer composition.

6) The copolymerization reaction gives 1:1 copolymer independently of polymerization time.

In Fig. 4, as in the case of alternating copolymer of isoprene and propylene, by comparing peak area of 8.32$\tau$ peak and that of 8.40$\tau$ peak, it is found that the structure of isoprene unit of the copolymer is mainly cis-1,4-structure. As in the case of the alternating copolymer of isoprene and propylene, the alternating copolymer of isoprene and butene-1 of the present invention is a new material.

The following results support the conclusion that the copolymer obtained in Experiment 1 of Example 25 is an alternating copolymer of isoprene and pentene-1.

1) In the infra-red spectrum of the copolymer (Fig. 5), there can be seen no peak near 909 $cm^{-1}$. Therefore, it is concluded that microstructure of isoprene unit of the copolymer is substantially composed of 3,4- and 1,4-structures.

2) In Fig. 6, measuring the ratio of peak area of the triplet at 4.8$\tau$ to half of that of the weak peak at 5.3$\tau$, the ratio of 1,4-structure to 3,4-structure is found to be 94/6.

3) It is found that the composition of the copolymer according to the NMR analysis substantially agrees well with the calculated value for the 1:1 copolymer of isoprene and pentene-1. The method for measuring the copolymer compositions was applied as was used in the case of alternating copolymer of isoprene and butene-1.

4) In Fig. 6, there can be seen substantially no peak at 7.95$\tau$ corresponding to 1,4-isolated value for the 1:1 copolymer of pentadiene-1,3 and propylene.

5) The copolymerization reaction gives 1:1 copolymer over a wide range of initial monomer composition.

6) The copolymerization reaction gives 1:1 copolymer independently of polymerization time.

In Fig. 6, as in the case of alternating copolymer of isoprene and propylene, by comparing peak area of 8.32$\tau$ peak and that of 8.40$\tau$ peak, it is found that the structure of isoprene unit of the copolymer is mainly cis-1,4-structure.

The alternating copolymer of isoprene and pentene-1 is also found to be a new material.

### Example 26.

The usual, dry, air-free technique was employed and 2.0 milliliters toluene and varying amounts of organic titanium compound were put into 25 milliliter glass bottles at 25°C. Then, the bottles were held in a low temperature bath at −78°C (it corresponds to catalyst preparation temperature in Table 17) and 0.6 milliliter organoaluminum compound solution in toluene (1 molar solution) and a mixture of 0.4 milliliters liquid propylene, 0.6 milliliter liquid cis-pentadiene-1,3 and 1.0 milliliter toluene were put successively into the bottles also employing the usual, dry, air-free technique. Thereafter, the bottles were sealed and the contents allowed to copolymerize at −40°C for 110 hours. The results were summarized in Table 17.

TABLE 17

| Exp. No. | Catalysts | | | | Catalyst preparation temperature (°C) | Polymerization conditions | |
|---|---|---|---|---|---|---|---|
| | Organoaluminium compound (mmol) | | Organic titanium compound (mmol) | | | Temperature (°C) | Time (hr.) |
| 1 | $Al(i-Bu)_3$ | 0.6 | $TiCl_2(O\overset{O}{\overset{\Vert}{C}}CH(CH_3)CH_3)_2$ | 0.2 | −78 | −40 | 110 |
| 2 | $Al(i-Bu)_3$ | 0.6 | $TiCl_3O\overset{O}{\overset{\Vert}{C}}C_6H_5$ | 0.2 | −78 | −40 | 110 |
| 3 | $AlEt_3$ | 0.6 | $TiCl_3O\overset{O}{\overset{\Vert}{C}}C_6H_5$ | 0.2 | −78 | −40 | 110 |
| 4 | $Al(i-Bu)_3$ | 0.6 | $O[TiCl_2O\overset{O}{\overset{\Vert}{C}}C_6H_5]_2$ | 0.1 | −78 | −40 | 110 |

TABLE 17 (continued)

| Exp. No. | Alternating copolymer of pentadiene and α-olefin | | | |
|---|---|---|---|---|
| | Yield (g) | Microstructure of pentadiene unit | | |
| | | cis-1,4 % | trans-1,4 % | 1,2 % |
| 1 | 0.02 | 8 | 92 | 0 |
| 2 | 0.23 | 9 | 91 | 0 |
| 3 | 0.15 | 10 | 90 | 0 |
| 4 | 0.18 | — | — | — |

The following results support the conclusion that the copolymer is an alternating copolymer of pentadiene-1,3 and propylene.

1) In the infra-red spectrum of the pentadiene-propylene copolymer (Fig. 9), it is found that microstructure of pentadiene unit of the copolymer is substantially 1,4-structure.

2) In the NMR spectrum of the copolymer (Fig. 10), the triplet at $4.7\tau$ is ascribed to the protons directly attached to the double bond of pentadiene unit showing 1,4-structure.

3) Copolymer compositions were determined as follows:

If A is peak area of the triplet at $4.7\tau$ and C is peak area of all the peaks appearing in the region from $7.5\tau$ to $9.5\tau$, the molar ratio of pentadiene to propylene in the copolymer can be shown by the following equation;

$$\frac{\text{pentadiene}}{\text{propylene}} = \frac{A/2}{(C-3A)/6} = \frac{3A}{C-3A}$$

It is found that the composition of the copolymer according to the NMR analysis substantially agrees well with the calculated value for the 1:1 copolymer of pentadiene-1,3 and propylene.

4) The copolymerization reaction gives 1:1 copolymer over a wide range of initial monomer composition.

5) The copolymerization reaction gives 1:1 copolymer independently of polymerization time.

6) Although the greater part of the 1,4-structure units of pentadiene-1,3 is trans-1,4, crystallization sensitive bands of trans-1,4-polypentadiene at 781, 866, 939, 1025 $cm^{-1}$ scarcely be found in Fig. 9.

7) In the NMR spectrum of amorphous polypropylene, a doublet ascribing to methyl group appears at $9.11\tau$ and $9.12\tau$. On the other hand, in Fig. 10, the doublet shifts to $9.04\tau$ and $9.15\tau$. This means that the doublet is ascribed to methyl group of propylene unit of alternating copolymer of pentadiene-1,3 and propylene.

The alternating copolymer of pentadiene-1,3 and propylene could not be prepared by the organoaluminum-vanadium compound type catalyst system.

The alternating copolymer is also considered to be a new material.

The special feature of the structure of alternating copolymer of pentadiene-1,3 and propylene prepared by the process of this invention is as follows:

a. Microstructure of pentadiene-1,3 unit of the alternating copolymer is 1,4-structure.

b. The greater part of the 1,4-structure units of pentadiene-1,3 is trans-1,4 structure.

c. Existence of 1,2-structure unit of pentadiene-1,3 can scarcely be detected by its infra-red spectrum.

Example 27.

The usual, dry, air-free technique was employed and 2.0 milliliters toluene, 0.2 millimole organic titanium compound and 0.1 millimole halogen compound were put successively into 25 milliliter glass bottles at 25°C. Then, the bottles were left alone at 25°C for 10 minutes. Thereafter, the bottles were held in a low temperature bath at −78°C (it corresponds to catalyst preparation temperature) and 0.6 millimole organoaluminum compound solution in toluene (1 molar solution) and a mixture of 0.4 milliliter liquid propylene, 0.6 milliliter liquid cis-pentadiene-1,3 and 1.0 milliliter toluene were put successively into the bottles also employing the usual, dry, air-free technique. Then, the bottles were sealed and the contents allowed to copolymerize at −40°C for 110 hours. The results were summarized in Table 18.

TABLE 18

| Exp. No. | Catalysts | | | Catalyst preparation temperature (°C) |
|---|---|---|---|---|
| | Organoaluminium compound (mmol) | Organic-titanium compound (mmol) | Halogen compound (mmol) | |
| 1 | $Al(i-Bu)_3$ 0.6 | $TiCl_2(O\overset{\overset{O}{\Vert}}{C}CH(CH_3)CH_3)_2$ 0.2 | $AlBr_3$ 0.1 | −78 |
| 2 | $Al(i-Bu)_3$ 0.6 | $TiCl_2(O\overset{\overset{O}{\Vert}}{C}CH(CH_3)CH_3)_2$ 0.2 | $C_4H_5COCl$ 0.1 | −78 |
| 3 | $AlEt_3$ 0.6 | $TiCl_3O\overset{\overset{O}{\Vert}}{C}CH_3$ 0.2 | $SbCl_5$ 0.1 | −78 |
| 4 | $Al(i-Bu)_3$ 0.6 | $O[Ti(O\overset{\overset{O}{\Vert}}{C}CH_3)_3]_2$ 0.2 | $SnCl_4$ 0.1 | −78 |
| 5 | $Al(i-Bu)_3$ 0.6 | $Ti(OCH(CH_3)CH_3)_2(O\overset{\overset{O}{\Vert}}{C}CH_3)_2$ 0.2 | $AlCl_3.OEt_2$ 0.1 | −78 |

TABLE 18 (continued)

| Exp. No. | Polymerization conditions | | Alternating copolymer of pentadiene & α-olefin | | | |
|---|---|---|---|---|---|---|
| | Temperature (°C) | Time (hr.) | Yield (g) | Microstructure of pentadiene | | |
| | | | | cis-1,4 (%) | trans-1,4 (%) | 1,2 (%) |
| 1 | −40 | 110 | 0.03 | 11 | 89 | 0 |
| 2 | −40 | 110 | 0.04 | 6 | 94 | 0 |
| 3 | −40 | 110 | 0.05 | — | — | — |
| 4 | −40 | 110 | 0.15 | 7 | 93 | 0 |
| 5 | −40 | 110 | 0.02 | — | — | — |

Example 28.

The usual, dry, air-free technique was employed and 2.0 milliliters toluene and 0.2 millimole

$$TiCl_3O\overset{\overset{O}{\|}}{C}C_6H_5$$

were put into a 25 milliliter glass bottle at 25°C. Then, the bottle was held in a low temperature bath at −78°C and 0.6 milliliter triisobutyl aluminum solution in toluene (1 molar solution) and a mixture of 0.6 milliliter liquid cis-pentadiene-1,3, 0.4 milliliter liquid hexene-1 and 1.0 milliliter toluene were put successively into the bottle also employing the usual, dry, air-free technique. Thereafter, the bottle was sealed and the contents allowed to copolymerize at −40°C for 110 hours. The copolymer thus obtained was determined as an alterating copolymer of cis-pentadiene-1,3 and hexene-1 by many facts, such as IR spectrum and NMR spectrum thereof. The yield of the alternating copolymer of cis-pentadiene-1,3 and hexene-1 soluble in diethyl ether and insoluble in MEK was 0.02g.

Example 29.

The usual, dry, air-free technique was employed and 2.0 milliliters toluene, 0.2 millimole

$$O[Ti(O\overset{\overset{O}{\|}}{C}CH_3)_3]_2$$

and 0.1 millimole stannic chloride were put successively into a 25 milliliter glass bottle at 25°C. Then, the bottle was left alone at 25°C for 10 minutes. Thereafter, the bottle was held in a low temperature bath at −78°C

and 0.6 milliliter triisobutylaluminum solution in toluene (1 molar solution) and a mixture of 0.6 milliliter liquid cis-pentadiene-1,3, 0.7 milliliter liquid hexene-1 and 1.0 milliliter toluene were put successively into the bottle also employing the usual, dry, air-free technique. Then, the bottle was sealed and the contents allowed to copolymerize at $-40°C$ for 110 hours. The yield of the alternating copolymer of cis-pentadiene-1,3 and hexene-1 soluble in diethyl ether and insoluble in MEK was 0.01g.

Example 30.

The usual, dry, air-free technique was employed and 7.0 milliliters toluene, 0.2 millimole

$$O[Ti(O\overset{\overset{O}{\|}}{C}CH_3)_3]_2$$

and 0.2 millimole $AlCl_3.OEt_2$ were put successively into a 25 milliliter glass bottle at 20°C. Then, the bottle was held in a low temperature bath at $-78°C$ and 1.0 milliliter triisobutylaluminum solution in toluene (1 molar solution) and a mixture of 1.0 milliliter liquid cis-pentadiene-1,3 and 1.0 milliliter propylene were put successively into the bottle also employing the usual, dry, air-free technique. Thereafter, the bottle was sealed and the contents allowed to copolymerize at 40°C for 24 hours. The yield of the alternating copolymer was 0.20g. The microstructure of pentadiene unit of the copolymer is as follows: cis-1,4: 20%, trans-1,4: 80%

WHAT WE CLAIM IS:—

1. A process for preparing an alternating copolymer of a $C_4$—$C_{12}$ conjugated diene and an $\alpha$-olefin having the general formula of $CH_2=CHR$ wherein R represents a $C_1$—$C_{12}$ hydrocarbon radical selected from alkyl, cycloalkyl, aryl and aralkyl radicals which comprises contacting said conjugated diene and said $\alpha$-olefin in the liquid phase with a catalyst composed of (A) an organoaluminum compound having the general formula of $AlR_3$ wherein R is as defined above and (B) an organic titanium compound having the

$$TiXO\overset{\overset{O}{\|}}{C}R$$

(R is as defined above and X is halogen) structure in the molecule.

2. A process as claimed in claim 1 wherein a halogen, a halogen compound (other than the organic titanium compound) or a mixture thereof is further included as a component of the catalyst.

3. A process as claimed in claim 1 or 2 wherein the atomic ratio of aluminum atom contained in the organoaluminum compound two titanium atom contained in the organic titanium compound is within a range from 1 to 200 ($1<Al/Ti<200$).

4. A process as claimed in claim 3 wherein said ratio is within a range from 2 to 100 ($2<Al/Ti<100$).

5. A process as claimed in claim 2 wherein the atomic ratio of titonium atom contained in the organic titanium compound to the halogen or halogen atom contained in the halogen compound is within a range of from 0.01 to 20 ($0.01<Ti/X<20$).

6. A process as claimed in claim 5 wherein said ratio is within a range from 0.02 to 10 ($0.02<Ti/X<10$).

7. A process as claimed in any one of claims 1—6 wherein the molar ratio of said diene to said $\alpha$-olefin in the initial monomer composition is within a range from 10:1 to 1:100 ($10/1>$diene/olefin$>1/100$).

8. A process as claimed in claim 7 wherein said ratio is within a range from 5:1 to 1:50 ($5/1>$diene/olefin$>1/50$).

9. A process as claimed in any one of claims 1—8 wherein said organoaluminum compound and said organic titanium compound are mixed at a temperature within a range from $-100°C$ to $+100°C$.

10. A process as claimed in claim 9 wherein said temperature is within a range from $-78°C$ to $+50°C$.

11. A process as claimed in claim 2, 5 or 6 wherein said halogen, halogen compound or a mixture thereof is mixed with the other catalyst components at a temperature within a range from $-100°C$ to $+100°C$.

12. A process as claimed in claim 11 wherein said temperature is within a range from $-78°C$ to $+50°C$.

13. A process as claimed in any one of claims 1—12 wherein the polymerization reaction is carried out at a temperature within a range from $-100°C$ to $+100°C$.

14. A process as claimed in claim 13 wherein said temperature is within a range from $-78°C$ to $+50°C$.

15. An alternating copolymer of a $C_5$—$C_{12}$ conjugated diene and an $\alpha$-olefin having the general formula of $CH_2=CHR$ wherein R represents a $C_1$—$C_{12}$ hydrocarbon radical selected from alkyl, cycloalkyl, aryl and aralkyl radicals.

16. An alternating copolymer as claimed in claim 15 wherein said conjugated diene is isoprene.

17. An alternating copolymer as claimed in claim 16 characterized in that (a) more than 85% of isoprene units in the copolymer are connected in 1,4-structure, (b) more than 75% of the isoprene units having 1,4-structure are connected in cis-1,4-configuration and (c) 1,2-structure isoprene units are substantially absent from its infra-red spectrum and its nuclear magnetic resonance spectrum.

18. An alternating copolymer as claimed in

claim 15 wherein said conjugated diene is pentadiene-1,3.

19. An alternating copolymer as claimed in claim 18 characterized in that (a) the microstructure of pentadiene-1,3 units in the copolymer is essentially in 1,4-structure, (b) more than 75% of the pentadiene units having 1,4-structure are connected in trans-1,4-configuration and (c) 1,2-structure pentadiene units are substantially absent from its infrared spectrum and its nuclear magnetic resonance spectrum.

20. A process for preparing an alternating copolymer of butadiene and an $\alpha$-olefin of the formula $CH_2{=}CHR$ (where R is phenyl, or an alkyl radical or a cycloalkyl radical with up to 8 carbon atoms) by contacting butadiene and the $\alpha$-olefin in liquid phase in the presence of a three component catalyst comprising an organoaluminium compound represented by the general formula $AlR'_3$ (wherein R' represents an alkyl, aryl or cycloalkyl radical), an organic titanium compound having a

$$\mathrm{Ti{-}O\overset{\displaystyle O}{\overset{\|}{C}}R'}$$

linkage (R' is as defined above) and having no Ti—X linkage (X represents halogen) and a halogen or halogen containing compound.

21. A process for preparing an alternating copolymer of butadiene and an $\alpha$-olefin of the formula $CH_2{=}CHR$ (where R is phenyl, or an alkyl radical or a cycloalkyl radical with up to 8 carbon atoms) by contacting butadiene and the $\alpha$-olefin in liquid phase in the presence of a catalyst comprising an organoaluminum compound represented by the general formula $AlR'_3$ (wherein R' represents an alkyl, aryl or cycloalkyl radical) and an organic titanium compound having an

$$\mathrm{X{-}Ti{-}O\overset{\displaystyle O}{\overset{\|}{C}}R'}$$

linkage (X represents halogen and R' is as defined above).

22. A process as claimed in claim 21 in which the catalyst also contains a halogen or a halogen containing compound (other than the organic titanium compound).

23. A process for preparing an alternating copolymer of isoprene and an $\alpha$-olefin of the formula $CH_2{=}CHR$ (where R is phenyl, or an alkyl radical or a cycloalkyl radical with up to 8 carbon atoms) by contacting isoprene and the $\alpha$-olefin in liquid phase in the presence of a three component catalyst system comprising an organoaluminium compound represented by the general formula $AlR'_3$ (wherein R' represents an alkyl, aryl or cycloalkyl radical), an organic titanium compound having a

$$\mathrm{Ti{-}O\overset{\displaystyle O}{\overset{\|}{C}}R'}$$

linkage (R' is as defined above) and having no Ti—X linkage (X represents halogen) and a halogen or halogen containing compound).

24. A process for preparing an alternating copolymer of isoprene and an $\alpha$-olefin of the formula $CH_2{=}CHR$ (where R is phenyl, or an alkyl radical or a cycloalkyl radical with up to 8 carbon atoms) by contacting isoprene and the $\alpha$-olefin in liquid phase in the presence of a catalyst comprising an organoaluminium compound represented by the general formula $AlR'_3$ (wherein R' represents an alkyl, aryl or cycloalkyl radical) and an organic titanium compound having

$$\mathrm{X{-}Ti{-}O\overset{\displaystyle O}{\overset{\|}{C}}R'}$$

linkage (X represents halogen and R' is as defined above).

25. A process as claimed in claim 24 in which the catalyst also contains a halogen or a halogen containing compound (other than the organic titanium compound).

26. A process for preparing an alternating copolymer of 1,3-pentadiene and an $\alpha$-olefin of the formula $CH_2{=}CHR$ (where R is phenyl, or an alkyl radical or a cycloalkyl radical with up to 8 carbon atoms) by contacting 1,3-pentadiene and the $\alpha$-olefin in liquid phase in the presence of a three component catalyst system comprising an organoaluminuium compound represented by the general formula $AlR'_3$ (wherein R' represents an alkyl, aryl or cycloalkyl radical), an organic titanium compound having a

$$\mathrm{Ti{-}O\overset{\displaystyle O}{\overset{\|}{C}}R'}$$

linkage (R' is as defined above) and having no TiX linkage (X represents halogen) and a halogen or a halogen containing compound.

27. A process for preparing an alternating copolymer of 1,3-pentadiene and an $\alpha$-olefin by contacting 1,3-pentadiene and the $\alpha$-olefin of the formula $CH_2{=}CHR$ (where R is phenyl, or an alkyl radical or a cycloalkyl radical with up to 8 carbon atoms) in liquid phase in the presence of a catalyst comprising an organoaluminium compound represented by the general formula $AlR'_3$ (wherein R' represents an alkyl, aryl or cycloalkyl radical) and an organic titanium compound having

$$\mathrm{X{-}Ti{-}O\overset{\displaystyle O}{\overset{\|}{C}}R'}$$

linkage (X represents a halogen and R' is as defined above).

28. A process as claimed in claim 27 in which the catalyst also contains a halogen or a halogen containing compound (other than the organic titanium compound).

29. A process for preparing an alternating copolymer of an $\alpha$-olefin and a conjugated diene as claimed in claim 1 and substantially as hereinbefore described with reference to and as illustrated in the foregoing examples.

30. An alternating copolymer of an $\alpha$-olefin and a conjugated diene as claimed in claim 15 and substantially as hereinbefore described with reference to and as illustrated in the foregoing examples.

31. An alternating copolymer as claimed in claim 15 and substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, L1 3AB,
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1341275 COMPLETE SPECIFICATION

12 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

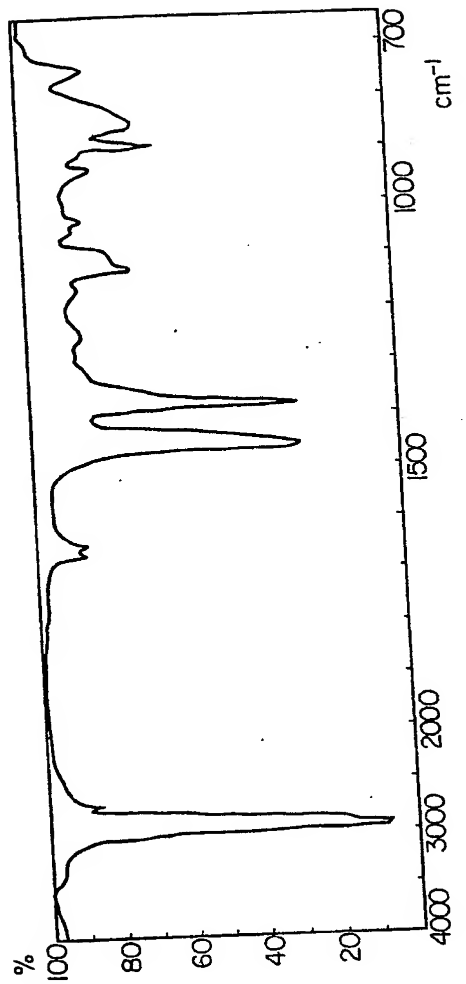
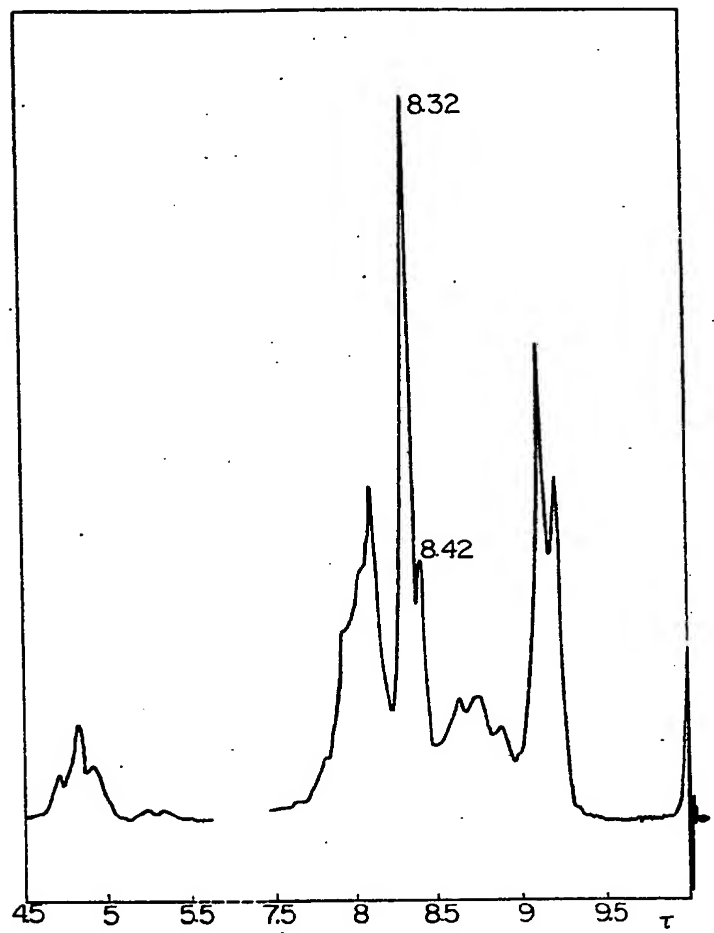



Fig. 1

Fig. 2



1341275 COMPLETE SPECIFICATION

12 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 3

Fig. 3

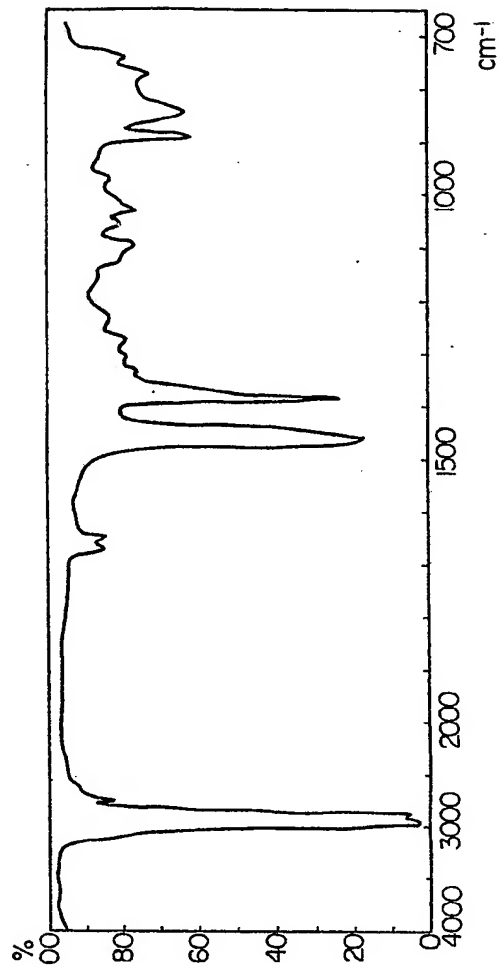
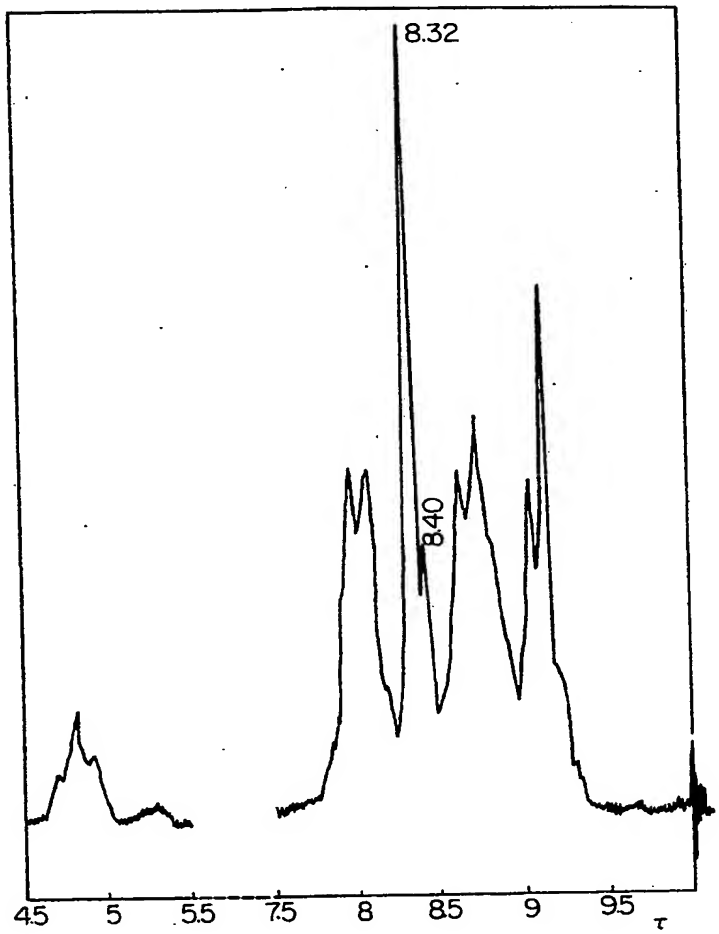


Fig. 4



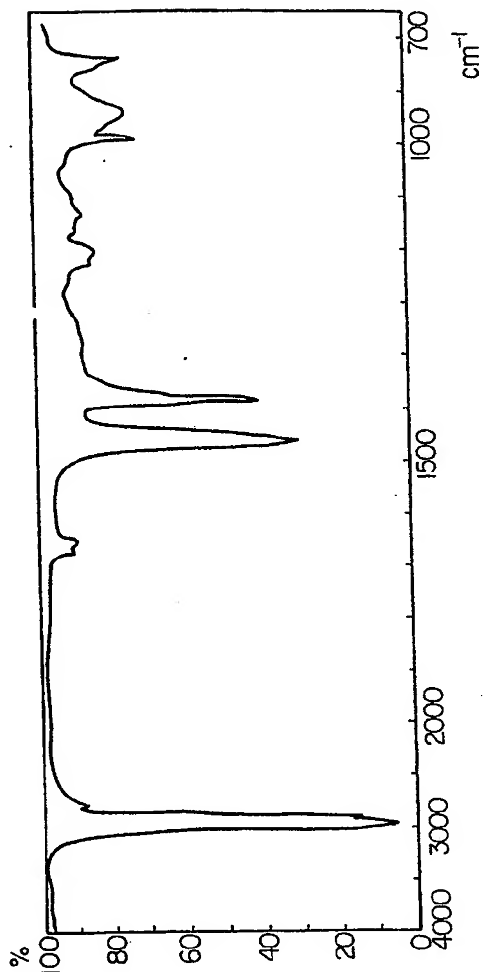
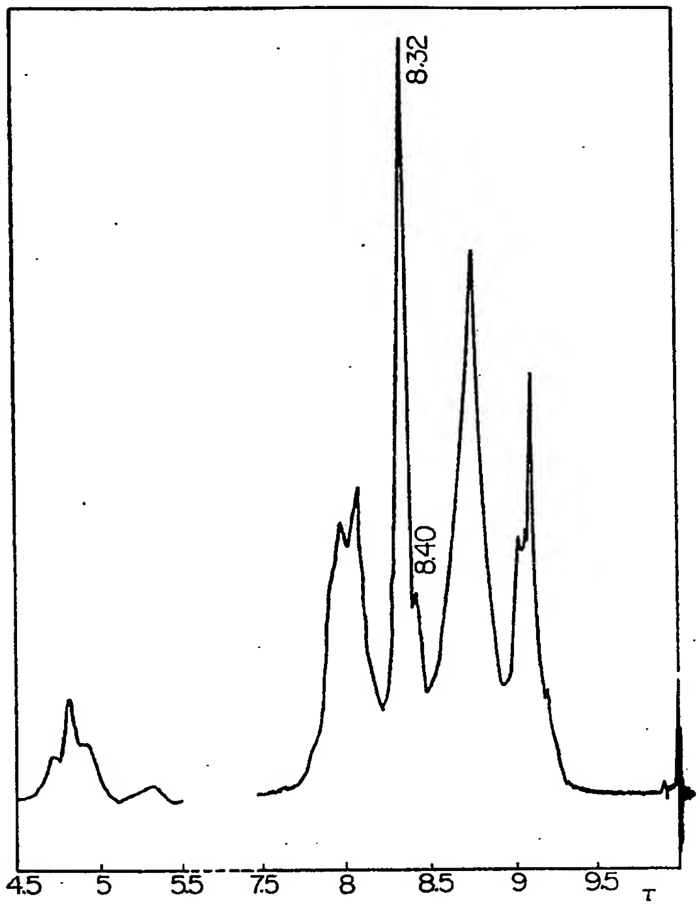



*Fig. 5*

Fig. 6



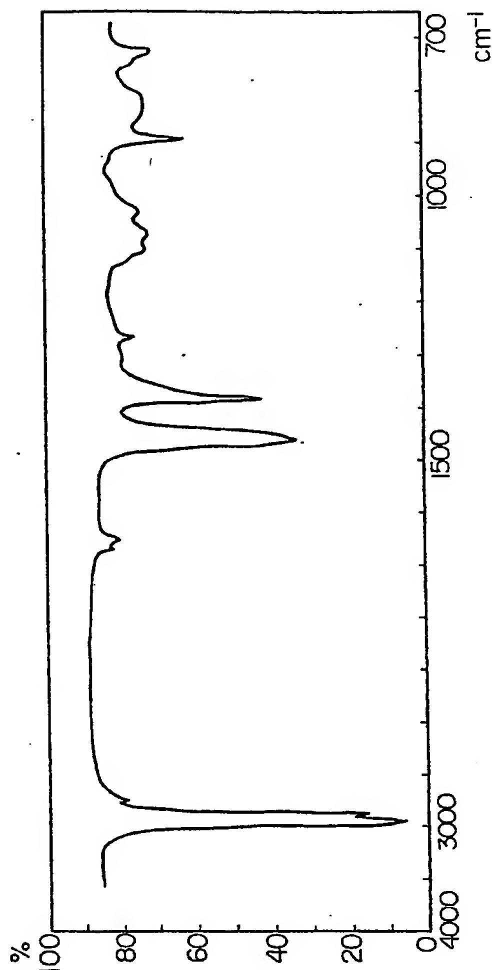
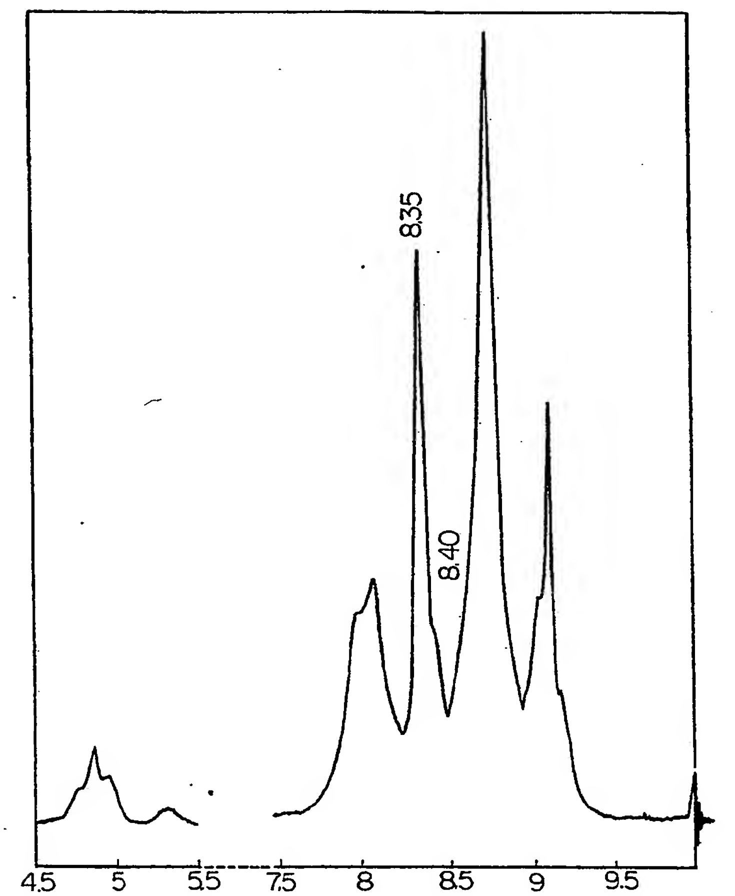



*Fig. 7*

Fig. 8



1341275 COMPLETE SPECIFICATION

12 SHEETS This drawing is a reproduction of the Original on a reduced scale

Sheet 9

Fig. 9

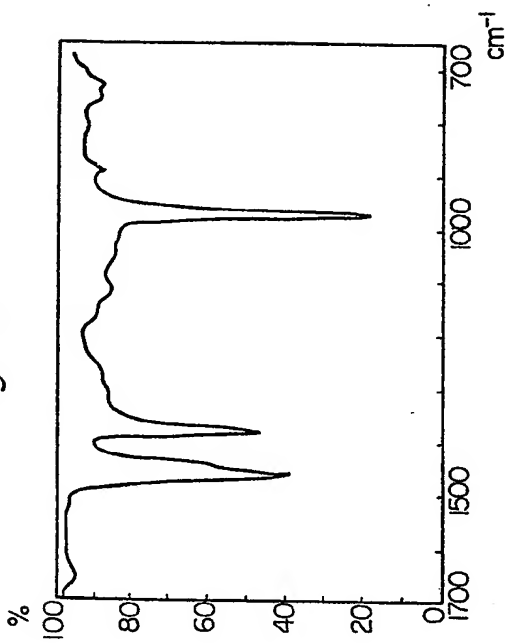


Fig. 10

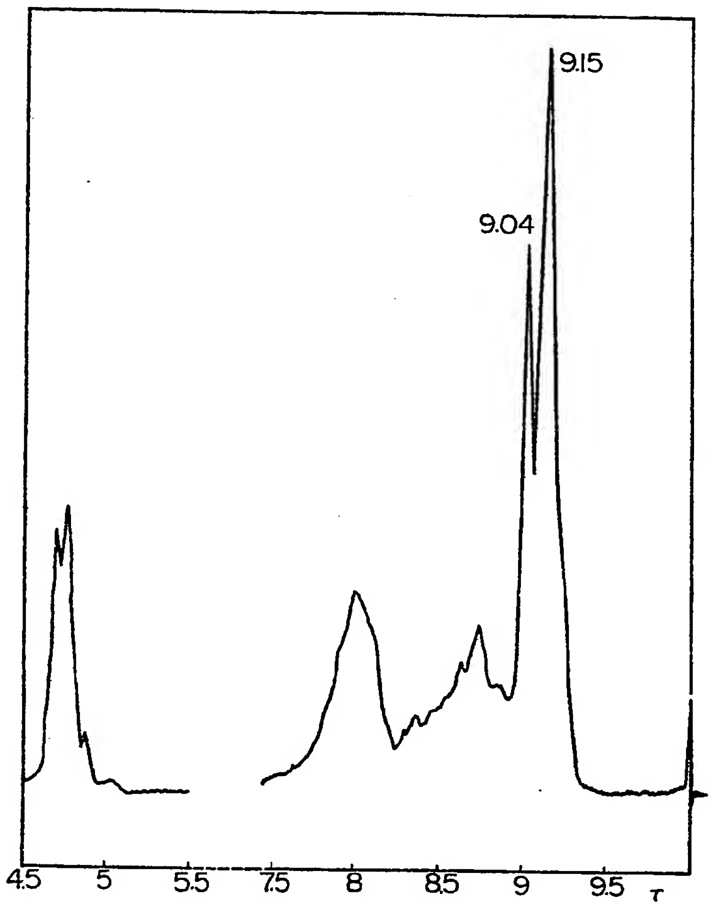


*Fig. 11*

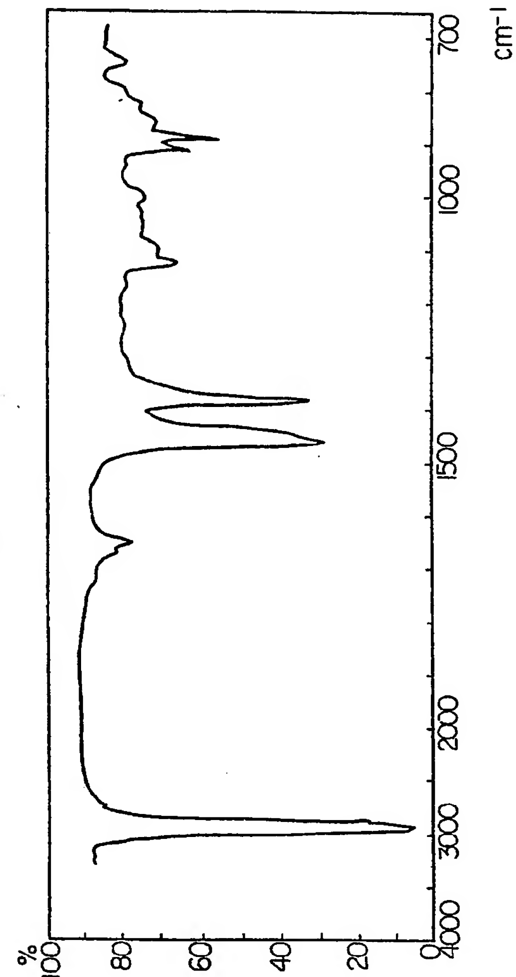


Fig. 12